## Neutron powder diffraction of minerals at high pressures and temperatures: some recent technical developments and scientific applications

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**Abstract:** The application of neutron powder diffraction to the study of mineral behaviour at high temperature and high pressure is reviewed. The characteristics of neutrons that make them particularly amenable to such studies are outlined, and recent technological developments in the attainment of extreme sample environments are discussed. These developments include the design of new high-pressure cells, hydrothermal cells, and furnaces that allow *in situ* diffraction under extreme conditions. The application of this technology to problems of order-disorder in minerals is illustrated in a series of recent examples.

Key-words: neutron diffraction, phase transition, high pressure, high temperature, order-disorder.

### Introduction

Neutron diffraction is a particularly useful method for the in situ study of mineral crystal structures for several reasons. Being uncharged nucleons, neutrons can penetrate deep into solids. This means that, when tuned in energy such that their wavelengths match those of inter-atomic spacings, they are able to provide detailed structural information of an entire bulk sample. The methods of generation of neutrons for mineralogical research are described elsewhere in this volume, and once generated (either at a reactor or spallation source) the energy of the neutron, or its velocity, may be selected and modified using moderators and monochromators designed to suit a particular diffraction experiment. For example, neutrons with an energy of 80 meV have a corresponding velocity of 4000 ms<sup>-1</sup>, which is equivalent to a wavelength of 1 Å, the atomic length scale. Neutrons have been used for research into mineral behaviour on many occasions, as may be judged from the accompanying paper by Pavese (2002), but the costs of producing them and the nature of the way that science must be carried out at a neutron source means that their adoption is nowhere near as widespread as, say, X-rays. However, neutrons have a large number of significant advantages for mineralogical research. For example, the diffraction of neutrons from solids is not generally limited to near-surface scattering in the way that of laboratory X-rays tend to be, since the neutron-absorption crosssection of most atoms is quite small and the penetration is large. There are further benefits, that have been commented upon elsewhere, but that are worth reiterating here. Importantly for Earth Sciences, light elements such as H, N, O and C scatter neutrons relatively strongly, compared with other elements, and the scattering length of an atomic species is independent of atomic number. The scattering lengths for neutrons are, however, isotope dependent, which provides the possibility of selecting different isotopic compositions to engineer strong or weak scattering from any particular atomic species. Hence isotopic substitution has been used to good effect (Enderby *et al.*, 1987; Galoisy *et al.*, 2000) to obtain a detailed picture of the structure and the environment around a particular labelled species.

The underlying controls on the scattering of neutrons from matter can be considered in terms of the two mechanisms by which they are scattered from atoms (Bacon, 1975). The first involves the interaction of the incident neutron with the atomic nucleus via the strong nuclear force. The second mechanism arises from the interaction of the neutron spin with the magnetic moment of the atom (this gives rise to scattering that may be of a similar magnitude to the nuclear contribution, but which is very distinct in many ways). The nuclear interaction is the sum of potential scattering and of resonant scattering. The former is positive and a function of the nuclear mass or number. The latter, however, can be negative. If it is, and is also larger than the potential term, the scattering amplitude from the atom is negative, corresponding to a  $\pi$  phase shift on the incident wave. This negative resonant scattering can mean that nuclei of very similar atomic number may have sharply contrasting neutron-scattering lengths (Fig. 1). For example, H and D have scattering lengths of -3.74 and 6.67fm respectively (illustrating that even the scattering lengths for different isotopes of the same element may be hugely different). Both these values are large enough to make neutrons an ideal probe for the study of the structural

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Fig. 1. Variation in the scattering amplitude of neutrons and X-rays with atomic number (after Bacon, 1975).

behaviour of hydrogen in minerals (which is particularly important given that X-rays will generally struggle to provide the necessary information, especially in crystal structures where heavy atoms are present to dominate the scattering). However, since incoherent neutron scattering from H is very large (raising the background in a diffraction pattern) but that from D is not, most workers attempt to deuterate hydrogenous materials for neutron studies. If, however, the deuteration is incomplete and, say, a particular site in the important particular crystal structure of interest contains partial occupancies of H and D of 0.64 and 0.36, respectively, the result will be a site with zero net scattering, caused by the contrast matching of the constituents. This would be a disaster for any study of the nature of hydrogen in that mineral, and underlines the need to characterise one's deuterated sample (for example, by infrared spectroscopy), before taking it to a neutron source.

The application of neutron scattering to the study of Earth materials is rather less mature than its use in other branches of the physical sciences, but increasing recognition is now being given to the role it may play in solving problems of mineral behaviour. Particularly relevant to the study of cation ordering and mixing processes in minerals is the fact that since neutrons scatter from the nucleus of atoms, in contrast to X-rays, their scattering power does not depend upon the number of electrons surrounding the atom, but rather upon the nuclear cross-section. At an order-disorder process, where chemically similar atoms (which may also therefore tend to have similar X-ray scattering powers) substitute on crystallographic sites, this can be particularly valuable. For example, the nuclear scattering contrast for Mg and Al is almost five times greater for neutrons than the contrast in X-ray atomic scattering factors (Fig. 1). For Mn and Fe the difference is even more marked: the neutron-scattering contrast is more than 36 times greater than the X-ray-scattering contrast, since Mn has a negative neutron-scattering length while Fe's is large and positive, while their atomic-scattering factors differ in magnitude by less than 4 %. The neutron-scattering length for Ni can be tuned between positive and negative values. depending upon the isotopic composition, and this can be



Fig. 2. Observed and fitted diffraction patterns of ilmenite, collected on the  $90^{\circ}$  detectors of the POLARIS time-of-flight powder diffractometer at ISIS.

exploited to increase the contrast between Ni other elements, effectively at will. Thus, elements that are difficult to distinguish by X-ray diffraction can show huge contrasts in neutron diffraction experiments.

Aside from strong scattering contrasts between chemically similar pairs of substituting atoms, neutron diffraction provides further advantages that may be exploited in studies of high-temperature order-disorder. Since neutrons scatter from the nucleus, which occupies a tiny fraction of the volume of the crystal, the atoms are effectively point scatterers, and the fall-off in scattering power with scattering vector,  $Q = \frac{4\pi \sin\theta}{\lambda} = \frac{2\pi}{d}$  for Bragg diffraction) is negligible. Thus, diffraction data may be obtained out to high scattering vectors (corresponding to small d-spacings), and complex structures may confidently and routinely be refined using total pattern fitting Rietveld methods (Rietveld, 1968) with high precision and accuracy (Fig. 2). This same characteristic has been used for the study of both short- and long-range order in minerals using total scattering methods (Dove *et al.*, 2000b; Gaskell, 2000; Harris et al., 2000; Keen & Dove, 2000).

Combining these facets of neutron powder diffraction (using fixed-geometry time-of-flight methods) with the fact that stable sample environments may be constructed around the sample without the worry of overly attenuating the incident and diffracted beams, we find that neutron time-of-flight powder diffraction is a powerful tool for observing structural changes at extremes of temperature. This much has been demonstrated by recent studies of the temperature dependence of inter-site partitioning of metal cations in olivines and spinels (Henderson *et al.*, 1996; Redfern *et al.*, 1996, 1997, 1998, 1999; Harrison *et al.*, 1998, 2000), and the work on more complex hydrous silicates that is presented below.

Furthermore, the effect of scattering length contrast matching of has been exploited to great positive effect in the construction of components from which one would like zero coherent elastic scattering, as is done for the alloy commonly pronounced as "tizer". This disordered alloy, 66 at.% Ti and 34 at.% Zr, is of a composition at which the positive scattering from Zr is exactly compensated by the negative scattering from Ti. As such, pressure-cell or other components can be constructed using Ti<sub>66</sub>Zr<sub>34</sub> and diffraction patterns can then be collected from samples contained within the cell, with no contribution from coherent elastic scattering in the diffraction pattern obtained arising from the  $Ti_{66}Zr_{34}$  components. Another notable metal in this regard is vanadium, which has a very low neutron-scattering length and which is, therefore, used to make sample canisters ("van. cans") and furnace elements. We shall see the importance of the adoption of these materials in the discussion of high-pressure and high-temperature neutron diffraction science and technology that follows below.

#### **High-pressure neutron diffraction technology**

Much of the recent motivation for conducting highpressure neutron powder diffraction has come from the desire to understand the behaviour of ices such as  $H_2O$ , NH<sub>3</sub> and CH<sub>4</sub> at the conditions of planetary interiors, and as such it sits firmly within the realm of mineralogy. While synchrotron X-ray diffraction at third-generation sources now allows diffraction from these materials to pressures beyond 100 GPa, thus far it has been used for little more than the measurement of cell-parameter variations and the determination of equations of state. Better data are needed if structural information, in particular the measurement of X-H distances in planetary ices and minerals, is to be obtained. The sensitivity of the neutron to H (or more particularly D) makes it an ideal tool for the study of the crystalline phases thought to comprise the interiors of large Jovian-kind planets at pressures of greater than 10 GPa. However, the low flux at most diffractometers and the small absolute-scattering cross-section leads to low count rates for neutron powder diffraction compared with X-ray diffraction, even from laboratory X-ray sources. For highpressure diffraction, certainly above the 0.5 GPa or so attained in gas cells, the apertures through which neutrons can pass from source to sample and then on to detectors are rather restricted, and beams must be tightly collimated to reduce the scattering contributing to the background and the scattering of contaminants (cell components other than the sample). Furthermore, any apertures that do exist are often highly attenuating. As a result, scattering from a sample held in a high-pressure apparatus is commonly around one tenth that obtained from the same volume of sample measured in an unrestricted ambient experiment. In addition, high pressures are usually obtained only by applying forces across small areas, imposing a limit on the size of the sample which may be held under pressure. Socalled "large volume" high-pressure apparatus typically contains samples with 25 to 50 mm<sup>3</sup> of material. This places a further restriction upon the rate at which one may collect data at high pressure. Recent progress in the field has been documented by Klotz et al. (1995) who point to the development of ultrahard materials, press design, the intensity of pulsed neutron sources, and the reduction of background with effective collimation as all being important in the development of high-pressure neutron powder diffraction.

The longest-standing type of high-pressure cell that has been used for neutron powder diffraction is the pistoncylinder cell (Fig. 3) designed by McWhan (1984). In this device the diffracted neutrons have to pass through the pressure cylinder, and in this case the size of the Bragg reflections from the sample may be of a similar magnitude to that of the reflections from the surrounding pressure cylinder. One route by which scattering from the pressure apparatus may be avoided is the use of careful collimation. In particular, high-pressure powder-diffraction experiments at time-of-flight scattering instruments can take advantage of the 90° scattering geometry, in which the scattering volume "seen" by the detectors is located wholly within the sample and contains no contribution from the pressure cell (Hull et al., 1997). In this case, hard encasement material may be employed for the pressure cylinder, and Walter (1984) has shown that the McWhan cell may be used to attain pressures up to 3.5 GPa using supported Al<sub>2</sub>O<sub>3</sub> cylinders.





Fig. 4. Schematic diagram of the anvil arrangement for the Paris-Edinburgh cell, showing the internal heating apparatus developed by Le Godec *et al.* (2001).

Fig. 3. Schematic diagram of the McWhan pressure cell, with the pistons shown in solid black.

It is worth discussing the approaches that can be taken towards collimating out the unwanted scattering from furnace or pressure-cell components at this point. In the case of diffraction at reactor sources, where angle-dispersive detectors are typically used with monochromatic radiation, contamination of the diffraction signal from the pressure jacket of a McWhan cell (for example) could be collimated out by trivial 90° scattering, but not when employing area- or position-sensitive detectors. As noted above, traditionally, the spatial resolution required to remove contributions that do not arise from the sample has been achieved by the use of a collimated incident beam, and a single slit (aperture) in the diffracted beam. This method has the advantage of being cheap and straightforward to implement. It does mean, however, that only a very small fraction of scattering space is being probed at any one time, and the solid angle of diffraction is very limited. Constantwavelength instruments employing this method are characterised by very slow count rates for the entire diffraction pattern. The advantages provided by area- and positionsensitive detectors are lost. An approach that circumvents these problems is provided by the use of radial collimators. These restrict the field of view of the detector onto a small region (a few centimetres or less) within the specimen, the gauge volume, and provide a means of exploiting large-area detectors without compromising the precision with which that volume is defined. When used on time-of-flight instruments the effect is to increase the count rate. If used on continuous, reactor sources, the technique enables a wider range of the diffracted spectrum to be recorded, increasing both the effective count rate and the information obtainable from the instrument. Radial collimators were first introduced by Wright *et al.* (1981), who described the cylindrical assembly of high-divergence slits, resembling a venetian blind, typically employed. When placed a short distance from the sample these permit the detector to collect scattering from the sample or a volume very close to it. Parasitic scattering from cryostats or furnaces enclosing the sample is absorbed by the slits. By combining their use with zeroscattering alloy components, such as those made from  $Ti_{66}Zr_{34}$ , one may get effective data from high-pressure and high-temperature apparatus at reactor sources, as has been described by Knorr *et al.* (1999a) in their modification of the Kiel-Berlin pressure cell.

The Kiel-Berlin cell (Knorr et al., 1997, 1999b) allows the development of high temperature as well as high pressure, providing the means to begin exploration of materials along the planetary geotherm, for example. This cell was developed for use at the Hahn-Meitner-Institute at Berlin, at which it is employed on an angle-dispersive powder diffractometer. It employs an internally-heated pressure cylinder, the heater being a thin graphite tube inserted between concentric tubes of pyrophyllite. The pistons, top and bottom, provide electrical contacts for a low-voltage high-current power supply. This apparatus was used to explore the temperature-pressure dependence of the phase transitions in TlD<sub>2</sub>PO<sub>4</sub>, a member of the KDP family of compounds between 300 and 400 K at pressures up to 1 GPa (Rios et al., 1999). A sequence of phase transitions from the room-temperature/pressure (RTP) monoclinic structure, through an orthorhombic phase, to a distinctive high-temperature/pressure monoclinic structure was observed both on heating and increasing pressure, and the structure was refined by the Rietveld method.

Work, led by groups from Edinburgh and Paris over the last decade, and carried out at ISIS, Rutherford Appleton

Laboratory, led to the development of the Paris-Edinburgh cell. In this cell, pressure is applied using two opposed anvils mounted in a way that permits use of sample volumes that are large enough to obtain neutron diffraction patterns good enough to yield useful structural information. This cell was adapted and designed for time-of-flight diffraction at fixed  $2\theta$ . In fact it uses the 90° scattering geometry, exploiting the ease with which such geometry can be used to collimate out non-sample scattering contributions. Its design is based around a portable hydraulic press which weighs no more than 50 kg but which still has a load capacity of around 250 tonnes. It is typically operated with opposed tungsten carbide toroidal anvils (Fig. 4), allowing a scattering volume for the sample of some 90 mm<sup>3</sup>. Using sintered diamonds, pressures can routinely be increased to 25 GPa, although 40 GPa has been achieved using a double-toroidal Ti<sub>66</sub>Zr<sub>34</sub> gasket, which begins to take this technique into a similar pressure regime as that explored by high-pressure synchrotron powder diffraction. Examples of minerals studied using the Paris-Edinburgh apparatus include brucite (Parise et al., 1994; Catti et al., 1995), muscovite (Catti et al., 1994), gypsum (Stretton et al., 1997), portlandite (Pavese et al., 1997), FeSi (Wood et al., 1995, 1996), hydrogarnet (Lager & Von Dreele, 1996), a variety of ice phases (Loveday et al., 1997), cristobalite (Dove et al., 2000a), FeS (Marshall et al., 2000), and Phase A (Kagi et al., 2000). Data collected in 1995 (Klotz et al., 1995) at 17 GPa on D<sub>2</sub>O, using the Paris-Edinburgh cell on the POLARIS time-of-flight diffractometer at ISIS, allowed measurements of the D-O bond lengths with an e.s.d. of  $\approx \pm 0.003$  Å after 8 hours' data collection. It is noteworthy that this is an order of magnitude improvement on the rate of data collection for a sample of the same material obtained by Jorgensen & Worlton (1985) using a McWhan cell at a much lower pressure of 2.6 GPa. Partly this is due to the improvement in neutron sources, partly to an increase in detector coverage (solid angle of diffracted radiation collected), but it also due to a notable improvement in the collimation and design of the presses used. Further improvements have been achieved since 1995, and one can anticipate that a further comparison in 2005 will demonstrate another magnitude step in the rate of data collection.

Until recently, the Paris-Edinburgh technology could only be used at ambient temperatures or lower. Zhao et al. (1999) first reported the development of an internally heated version of the Paris-Edinburgh cell, and used this for a study of the equation of state of molybdenum (Zhao et al., 2000). The ability to perform diffraction measurements at simultaneous high pressures and temperatures allows the possibility of performing in situ crystallographic studies of minerals under the conditions of the geotherm within the Earth's upper mantle. Recently Le Godec et al. (2001) reported on the further development of a Paris-Edinburgh cell with internal heating using methods that differ somewhat from those of Zhao et al. (1999). Their cell was tested to a pressure of 7 GPa simultaneously with temperatures of 1500°C. They also report the first results from the use of the internal-heating high-P/T Paris-Edinburgh cell in a study of deuterated brucite, which they

were able to compare with results from ambient-temperature high-pressure studies that had been conducted previously (Parise et al., 1994; Catti et al., 1995). One of the difficulties of high-P/T diffraction is the simultaneous measurement of temperature and pressure. Pressure can be measured using internal-pressure standards, and in principle thermocouples can be used for temperature measurement, as in the apparatus of Zhao et al. (1999). However, thermocouples tend only to survive pressurization if the sample can be pressed into a pellet prior to loading, and can be susceptible to breakage on the imposition of increasing pressure, causing delays associated with repair and reloading that are best avoided during a period of scheduled neutron beam time. Le Godec et al. (2001) have explored the possibility of using neutron radiographic methods to determine the temperature within the internally-heated cell, incorporating a Ta foil within the pressure cell and using a transmission monitor to measure the resonance absorption. The width of this absorption feature is a function of temperature, increasing in width with increasing temperature as a result of the Doppler effect (Fowler & Taylor, 1987; Mayers et al., 1989). This approach has been shown to be simple to implement, and gives accuracy in temperature measurement of better than  $\pm$  10 K at any pressure.

#### Hydrothermal and reaction cells

There have been a number of initiatives to develop apparatus to allow the study of materials held under hydrothermal conditions, or as they are reacting, using neutron diffraction. In the area of materials chemistry this is an important development for the study of materials undergoing hydrothermal crystallisation, while in mineralogy such apparatus opens the door to the study of hydrous (or, more properly, deuterated) clay minerals under the conditions of burial in sedimentary basins. Examples of the design and use of such cells include that of Turner *et al.* (1999), who describe a cell built to investigate catalysis and catalytic processes. The cell was designed for use at the ISIS spallation neutron source at the Rutherford Appleton Laboratory and operates in a dual manner, either under gas flows of controlled composition at low pressure (up to 5 bar) or at high vacuum (10<sup>-6</sup> mbar) at temperatures between 4 and 1273 K. In use, the cell is attached either to a furnace or cryofurnace centre-stick assembly. Walton *et al.* (1999) describe the design and use of a different pressure cell (also developed at ISIS) for the *in situ* study of hydrothermal crystallisation using time-resolved neutron diffraction. This allows the investigation of the kinetics and mechanism of crystallisation of zeolites and other microporous materials over a wide range of temperatures (25-250°C) under pressures up to 2.2 GPa. This cell has been used to study the hydrothermal crystallisation of sodium hydroxysodalite at the POLARIS time of flight diffractometer of ISIS (Walton et al., 1999). More recently, Whittaker et al. (2001) discuss apparatus for the study of the microwavedriven growth of particles in solution using in situ smallangle neutron scattering (SANS). This apparatus was used



Fig. 5. Temperature-dependence of cation ordering in several spinels and olivines, all measured by Rietveld refinement of neutron powder diffraction data.

to study the microwave-activated precipitation of iron oxide from solution, using a microwave cavity adapted to the geometric constraints of the diffractometer. Computercontrolled feedback to the microwave generator enabled the authors to maintain either constant pressure or temperature in the reaction vessel.

Within the Earth Sciences, de Siqueira *et al.* (1999) and Skipper *et al.* (2000) described the use of time-of-flight neutron diffraction in conjunction with isotopic substitution to obtain high-resolution structural data for clay-watercation systems, at elevated pressures and temperatures. They developed a hydrothermal sample environment from Ti-Zr alloy, to allow the study of clay-fluid interactions *in situ*, under hydrostatic fluid pressures of up to 0.2 GPa, and temperatures of up to 350°C, mimicking the environment of a sedimentary basin.

# Temperature-dependent studies of mineral behaviour

Typically, high-temperature neutron powder diffraction is easily implemented using vacuum furnaces with solid vanadium, niobium, or tantalum heating elements. For example, the RAL furnaces used at ISIS are constructed with cylindrical heating elements with a diameter of around 30 mm, which are surrounded within the vacuum apparatus with concentric heat shields. While vanadium furnaces may be operated to around 1400 K, the use of tantalum elements allows operation to around 2300 K.

The use of high-temperature neutron diffraction in mineralogy is exhaustively reviewed in the accompanying paper by Pavese (2002), and here I shall simply give some examples of the way in which such results may be applied

0.40

0.38

0.36

0.34

0.32

0.30

0.28

0.26

Degree of Order

0.1 K/s

1 K/s

10 K/s

100 K/s

to further our understanding of the nature of cation ordering in minerals. These examples are biased towards studies that I or my colleagues have been involved in, and are not intended to serve as a comprehensive review. For the latter the reader is encouraged to consult Pavese (2002). Low-temperature work is also discussed in his paper, but one aspect, that of magnetic scattering, is hardly touched upon. Here, I shall also indicate some of the studies that have, thus far, exploited the use of neutron diffraction in elucidating magnetic structure, but we shall start by considering cation order-disorder in minerals.

The temperature dependence of both convergent and non-convergent cation exchange in minerals, including sulphides (Grguric & Putnis, 1999; Grguric et al., 2000), olivines (Redfern et al., 1998), pyroxenes, amphiboles (Reece et al., 2000), micas (Pavese et al., 2000) and spinels has been the subject of a number of recent neutron diffraction studies using such furnaces. For olivines, these studies included the single-crystal studies of members of the forsterite-fayalite solid solution (Artioli et al., 1995; Rinaldi & Wilson, 1996, Rinaldi et al., 2001) and powder-diffraction studies of the same system (Redfern et al., 2001) as well as the Fe-Mn, Mg-Mn, and Mg-Ni systems (Henderson et al., 1996; Redfern et al., 1996, 1997, 1998). The high-temperature behaviour of Fe-Mg order-disorder appears to be complicated by crystal-field effects, which influence the site preference of Fe<sup>2+</sup> for M1 and M2, but the cation exchange of the Fe-Mn, Mg-Mn, and Mg-Ni olivines is dominantly controlled by size effects: the larger M2 site accommodating the larger of the two cations in each pair (Mn or Ni, in these cases). In all these experiments, the use of time-of-flight neutron powder diffraction allowed the measurement of states of order at temperatures in excess of 1000°C under buffered oxygen fugacities (especially important given the variable oxidation states that many of the transition metal cations of interest can adopt). Diffraction patterns were collected on the POLARIS diffractometer at the ISIS spallation source (Hull et al., 1992). The diffraction patterns of the Fe-Mn and Ni-Mn olivines were collected in four 30-minute time bins over two hours at each isothermal temperature step on heating, and over a single 30-minute period on cooling. Diffraction patterns of the Mg-Mn sample were collected over one-hour time intervals at each isothermal step on heating. Structural data were then obtained by Rietveld refinement of the whole patterns giving errors in the site occupancies of around 0.5 % or less. The low errors in refined occupancies result principally from the fact that the contrast between Mn (with a negative scattering length) and the other cations is very strong for neutrons.

All experiments showed the same underlying behaviour of the degree of cation order, defined by an order parameter Q. This can be modelled according to a Landau expansion for the free energy of ordering, of the type:

$$\Delta G = -hQ + \frac{a}{2}(T - T_c)Q^2 + \frac{b}{4}Q^4$$
, where *h*, *a*, *b* and *T*<sub>c</sub> are

material-dependent parameters and the order parameter, Q, describes the degree of cationic order/disorder over the two sites. This expression, chosen to describe the free-energy change due to ordering, is formally equivalent to the recip-



olivine. Variations in the cooling rate (shown) gives rise to different degrees of quenched-in order (after Redfern et al., 1997).

rocal solution model at lowest order, although the manner in which free energy is partitioned between entropy and enthalpy differs between the two approaches (Carpenter et al., 1994; Kroll et al., 1994). The Landau formulation essentially treats entropy as vibrational rather than configurational. Kroll et al. (1994) have shown that the addition of a configurational entropy term models the entropy at high Qmore accurately, in particular for the non-convergent ordering behaviour of Mg and Fe on M-sites in pyroxene. The same was found in neutron diffraction studies of orderdisorder in spinels and hematite-ilmenite oxides (Harrison et al., 1998, 2000; Harrison & Redfern, 2001).

In each case studied (Fig. 5) the order parameter remains constant at the start of the heating experiment, then increases to a maximum before following a steady decline with T to the highest temperatures. This general behaviour reflects both the kinetics and thermodynamics of the systems under study: at low temperatures the samples are not in equilibrium and reflect the kinetics of order-disorder, at high temperatures the states of order are equilibrium states, reflecting the thermodynamic drive towards hightemperature disorder. The initial increase in order results from the starting value being lower than equilibrium, and as soon as the temperature is high enough for thermally activated exchange to commence (on the time scale of the experiments), the occupancies of each site begin to converge towards the equilibrium order-disorder line. Using Ginzburg-Landau theory, which relates the driving force for ordering to the rate of change of order, one can obtain a kinetic and thermodynamic description of the nonconvergent disordering process from a single experiment (e.g., Redfern et al., 1997).

These studies of cation ordering in olivines have shown that, in most cases, the degree of M-site order measured at room temperature is an indication of the cooling rate of a sample, rather than the temperature from which it has



Fig. 7. Temperature dependence of the distribution coefficient of cation exchange,  $K_D$ , for  $(Ni,Mg)_2SiO_4$  olivines of two compositions (data of Henderson *et al.*, 2001).

cooled. Calculated Q-T cooling pathways for a Fe-Mn olivine are shown in Fig. 6, where it is evident that variations in cooling rate over several decades might be ascertained from the degree of order locked in at room



Fig. 8. T dependence of Q for members of the ilmenite-hematite solid solution, determined from neutron powder diffraction (solid symbols: Harrison *et al.*, 2000) and quench magnetization measurements (open symbols). Solid lines are fits using a modified Bragg-Williams model.

temperature. This indicates the potential for cation ordering in minerals to be employed in geospeedometry. However, it is clear that more complex cooling paths may reset the degree of order on re-heating. It would then be difficult to trace back a complex cooling history from a single measurement of Q at room temperature. In the case of these more complex cooling histories, M-site order measurements would have to be carried out in conjunction with other measurements using additional speedometers.

The influence of processes of intra-mineral partitioning (order-disorder) on inter-mineral partitioning in the olivine system has been pointed out by Bish (1981). His arguments are illustrated with new data (Henderson *et al.*, 2001) on the composition dependence and temperature dependence of Ni-Mg ordering in olivines (Fig. 7). The more magnesium-rich sample shows a higher degree of order, with Ni ordering onto M1. The *in situ* neutron diffraction studies that have been performed in recent years have allowed the temperature dependence of this ordering to be determined accurately to high *T*. In these cases *in situ* study has been essential, since high-temperature disordered states are often non-quenchable, due to the fast kinetics of cation exchange in structures such as olivines and spinels, and the unavoidable re-equilibration of samples on quenching from annealing conditions.

Another recent example was the study of members of the  $(FeTiO_3)_x(Fe_2O_3)_{1-x}$  solid solution (Harrison *et al.*, 2000; Harrison & Redfern, 2001). These minerals have large saturation magnetizations and contribute significantly to the palaeomagnetic record. Often such material is

observed to acquire self-reversed remnant magnetization. In all cases, the high-temperature  $R\overline{3}c$  to  $R\overline{3}$  cationordering transition plays a crucial role in determining the thermodynamic and magnetic properties. This transition involves the partitioning of Ti and Fe cations between alternating (001) layers of the hexagonal-close-packed oxygen sublattice. Above the transition temperature  $(T_c)$  the cations are distributed randomly over all (001) layers. Below  $T_c$  the cations order to form Fe-rich A-layers and Ti-rich B-layers. Harrison et al. (2000) carried out an in situ time-of-flight neutron powder diffraction study (Fig. 2) of synthetic samples of the  $(FeTiO_3)_x(Fe_2O_3)_{1-x}$  solid solution with compositions x = 0.7, 0.8, 0.9 and 1.0. The cation distributions were obtained directly from measurements of the site occupancies using Rietveld refinement of powder diffraction data. This is especially powerful in this case because of the very large neutron-scattering contrast between Ti and Fe. Furthermore, the use of large sintered samples heated in a vanadium furnace, allows confidence that the oxidation state of the sample does not change on heating. In this system, departures from the expected oxygen fugacity result in the precipitation of different phases, so it was possible to confirm the efficacy of the buffering of  $fO_2$ with the vanadium furnace. These measurements offered the first insight into the equilibrium cation-ordering behaviour of this system over this compositional range and allow one to observe simultaneously the changes in degree of order, spontaneous strain and the cation-cation distances as a function of temperature. An interpretation of the observations was possible, underlining the importance of the various long- and short-range ordering processes which operate. Values of the long-range order parameter, Q, are shown in Fig. 8. In all cases, the estimated standard deviation in O is smaller than the size of the symbols. The value of Q measured at room temperature represents the degree of order maintained after quenching the starting material from the synthesis temperature of 1300°C. For the ilmenite-rich samples the quenched starting material is almost fully ordered, with Q = 0.98 in all three cases. The data close to  $T_c$  can only be fitted with a critical exponent for the order parameter,  $\beta$ , which is of the order of 0.1, which does not correspond to any classical mean field Landau-type model. Instead, a modified Bragg-Williams model is required, that describes the free energy in terms of a configurational entropy alongside an enthalpy that contains

terms up to 
$$Q^4$$
, giving  $\Delta G = \mathbf{R}T \ln \Omega + \frac{1}{2}aQ^2 + \frac{1}{4}bQ^4$ .

The application of neutron powder diffraction to the study of the magnetic structure and behaviour of minerals has not been as extensively pursued as has the measurement of crystalline structure more generally. The use of intensities due to magnetic scattering to measure the temperature-dependent relationship between magnetic and cation ordering in ilmenites was described by Harrison & Redfern (2001). Here, the influence of cation order-disorder domain size and magnetic domain size was measureable from the widths of the associated reflections.

Earlier examples of the use of neutron diffraction for the study of magnetic structure at non-ambient conditions in minerals include those on the details of magnetic superlattices found in various members of the olivine family as described Ballet et al. (1987, 1989); Baron et al. (1999); Cox et al. (1969); Creer & Troup (1970); de Oliveira et al. (1991); Duc et al. (1969); Hagemann et al. (2000); Hove & O'Reilly (1972); Kato et al. (1995); Lottermoser et al. (1986); Nordblad et al. (1999); Schmidt et al. (1992, 1995); Tellefsen et al. (1983); Vincent & Bertaut (1973), amongst others! The applications of neutron diffraction to solving and characterising the quasi-linear magnetic ordering schemes seen at low temperature in pyroxenes and amphiboles have been discussed by Amthauer et al. (1998); Ghose et al. (1987, 1988); and Wiedenmann & Regnard (1986). The details of these studies cannot be discussed within the scope of this paper, but they serve as an indication of the potential for the application of neutron diffraction within this area.

#### In conclusion

From the many studies of order-disorder process in minerals that have now been conducted at both reactor and spallation sources, it has become clear that neutron diffraction techniques are invaluable for directly determining the long-range ordering characteristics of these important rock-forming minerals. Of special note is the possibility of determining the kinetics and thermodynamics of these processes simultaneously from one time-temperature study, which makes this method particularly powerful. In conclusion, it seems clear that the application of neutron diffraction to the study of minerals at extremes of temperature and pressure will continue to develop in the coming years. The opportunities afforded by the development of new spallation sources (the SNS at Oak Ridge, the second target station at ISIS, and the proposed European Spallation Source) as well as new reactor sources worldwide will inevitably include instruments with higher flux, allowing the study of faster processes, smaller samples as well as for samples held under increasingly extreme conditions. All of these advances are likely to significantly benefit mineral sciences.

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