Direct observation of spinodal decomposition in the magnetite-hercynite system by susceptibility measurements and transmission electron microscopy

UTE GOLLA-SCHINDLER,1,* HUGH ST.C. O’NEILL,2 AND ANDREW PUTNIS1

1Institute of Mineralogy, University of Münster, Corrensstrasse 24, 48149 Münster, Germany
2Research School of Earth Sciences, Australian National University, Canberra ACT 0200, Australia

ABSTRACT

The magnetic susceptibility and Curie temperatures $T_c$ have been investigated for a series of synthetic samples with solid-solution compositions ranging from pure magnetite (Fe$_3$O$_4$) to hercynite (FeAl$_2$O$_4$). The determined $T_c$ can be fitted by a straight line, which also fits the theoretical values for these end-members. With increasing hercynite concentration, susceptibility curves for one heating and cooling cycle become irreversible, indicating changes in the structural state of the samples during annealing. These changes occur in specific temperature ranges for each composition. For a sample of composition Mag$_{45}$Hec$_{55}$, irreversible changes occurring between about 200 and 300 °C are likely due to changes in the cation distribution, whereas above 300 °C, compositional fluctuations due to spinodal decomposition are evident. The exsolution mechanism has been investigated using energy-filtered transmission electron microscopy, which has allowed direct imaging of the compositional fluctuations consistent with the theoretical predictions of spinodal decomposition.

INTRODUCTION

Magnetic properties of oxide minerals are dictated by the superexchange interactions between the spin orientations of unpaired electrons. Therefore small changes in the chemical composition, the degree of cation order, or microstructure associated with exsolution or other chemical changes such as oxidation can introduce drastic changes in the magnetic properties of the bulk material. In natural rocks remanent magnetization occurs in various mineral systems, the most important of which are titanomagnetite (Fe$_3$O$_4$-Fe$_2$TiO$_4$) and titanohematite (Fe$_2$O$_3$-FeTiO$_3$) solid solutions. Both of these solid solutions are non-ideal. The composition modulation and size of fine precipitates resulting from exsolution during cooling control the magnetic properties (Harrison and Putnis 1996, 1997; Kasama et al. 2003).

It is experimentally difficult to study exsolution in the titanomagnetite solid solution due to the low solvus temperature (<500°C) and hence the slow kinetics. An ideal analogue system is the magnetite (Fe$_3$O$_4$)-hercynite (FeAl$_2$O$_4$) system, which has a miscibility gap to higher temperatures, forming a complete solid solution above 850 °C (Turnock and Eugster 1962). Petric et al. (1981) also determined the solvus from calculated cation distributions, which shows a good agreement in the maximum temperature but slight changes in the shape for non-intermediate compositions.

In this work we have used a series of synthetic samples with compositions ranging from pure magnetite to hercynite to investigate the behavior of the solid solution during annealing. We first investigated the magnetic susceptibility and determined $T_c$ for this binary solid solution system using a χ-bridge (Jelinek and Pokorny 1997). The χ-Bridge is extremely sensitive to small amounts of material with different $T_c$, such as would be produced by heterogeneities due to exsolution or oxidation processes. To study such processes during annealing and specifically to determine the exsolution mechanism it is necessary to investigate variations in the chemical composition at high spatial resolution.

The concept of two different mechanisms of exsolution was first introduced by Gibbs (1961) and is well established in the mineralogical literature. In nucleation and growth, compositional fluctuations are large in degree but small in extent while in spinodal decomposition, the compositional fluctuations are small in degree but large in extent. For the solid solution compositions for which the molar free energy of mixing has a positive curvature the exsolution mechanism is nucleation and growth but for a negative curvature the predicted exsolution mechanism is spinodal decomposition. Spinodal decomposition is a continuous process, in contrast to exsolution by nucleation and growth, which is a discontinuous process involving a large compositional change, an activation energy barrier and much slower kinetics. These two mechanisms have been recognized in minerals (e.g., Champness and Lorimer 1975) on the basis of textural features observed by transmission electron microscopy (TEM). However, the presence of sinusoidal compositional fluctuations formed during spinodal decomposition has not yet been demonstrated by microanalytical techniques (Weinbruch et al. 2003) and is generally inferred from the satellite reflections around Bragg diffraction spots. One of the aims of this paper is to verify spinodal decomposition by direct chemical analysis of compositional modulations.

In the early stages of exsolution, the size of the magnetite-rich and hercynite-rich domains is likely to be critically small for detection. This requires an investigation technique which allows detection of chemical information at low concentration.
differences resolved with a high spatial resolution. Analytical investigation of microstructures using energy-dispersive X-ray detectors in TEMs is well established, but the spatial resolution is limited by the interaction volume where the X-rays are produced. This may still be in the range of micrometers by using electron probes in the range of nanometer spot size. It is impossible to obtain information on the nanometer scale of exsolution phenomena by using these techniques, but sharp features will be blurred by the enlarged interaction volume of the X-rays.

Energy-filtered TEM (EFTEM), which uses the energy loss of the electrons to form an element map, is capable of providing reliable chemical compositional information with nanometer scale spatial resolution. The major factor limiting the attainable spatial resolution is the transfer function of the microscope. The detection limit is determined by the available signal to noise ratio. This is affected by the cross-section of the investigated material, i.e., by the energy and shape of the ionization edge and by the beam sensitivity of the specimen. Further effects influencing the attainable spatial resolution and detection limit include delocalization, life-time broadening, instrument instabilities, specimen drift and cross-talking of the atom columns (Batson et al. 2002; Lentzen et al. 2002; Muller and Grazul 2001). However, several investigations of such limitations of EFTEM using test specimens have shown that it is possible to detect monolayers and reach a spatial resolution of 1 nm (Jäger and Mayer 1995; Freitag and Mader 1999; Kurata et al. 2001). This means that structures down to a size of 1 nm are imaged with their original size and smaller features appear with a size of 1 nm blurred by different resolution limiting factors (Kasama et al. 2003; Groger et al. 2003).

**EXPERIMENTAL PROCEDURES**

The starting material for the experimental investigations was a series of synthetic samples with compositions ranging from pure magnetite to the non-magnetic end-member hercynite at compositional intervals of 10%. The samples were synthesized from a mixture of Fe₂O₃ and Al₂O₃ sintered for 48 hours at temperatures from 1300 to 1500 °C under appropriate CO/CO₂ atmospheres depending on the Fe/(Fe + Al) ratio. The sintering temperature was subsequently lowered to 1100 °C and the samples were held there for one hour before being quenched onto dry ice. The compositions (Table 1) were checked by electron microprobe analysis (Höfer et al. 1994). Lattice parameters were determined, as described in (O’Neill and Navrotsky 1984), using X-ray diffraction and an internal standard of NIST Si and AI₂O₃. The determination of the molar fraction of FeAl₂O₄-containing solid solutions because of the change in site-preference of Fe²⁺ as the cation distribution in the spinel solid solution goes from basically “inverse” at Fe₂O₃ to basically “normal” at FeAl₂O₄ (O’Neill and Navrotsky 1984).

The magnetic susceptibility measurements were performed with a dry argon atmosphere or an argon 10% hydrogen mixture pumped into the glass specimen tube.

**An Overview of Magnetic Susceptibility Measurements**

The inflection point of the susceptibility curve defines \( T_c \) and can be determined by the intersection of two straight lines, fitting the sharp drop and the high temperature range of the susceptibility curve (Harrison and Putnis 1999). Determining \( T_c \) for the whole range of synthetic specimens was limited by the temperature range of the \( \chi \)-Bridge and only concentrations to hercynite 80% could be measured. The measured \( T_c \) values (Fig. 1) can be fitted by a straight line, which also fits the theoretical values for hercynite and magnetite.

With increasing hercynite concentration, susceptibility curves

<table>
<thead>
<tr>
<th>Nominal composition ( (X_{Hc}) )</th>
<th>Composition electron microprobe ( (X_{Na}) )</th>
<th>Lattice parameter ( (\AA) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>NA</td>
<td>8.3970</td>
</tr>
<tr>
<td>0.1</td>
<td>0.099(7)</td>
<td>8.3698</td>
</tr>
<tr>
<td>0.2</td>
<td>0.206(15)</td>
<td>8.3469</td>
</tr>
<tr>
<td>0.3</td>
<td>0.287(13)</td>
<td>8.3270</td>
</tr>
<tr>
<td>0.4</td>
<td>0.371(14)</td>
<td>8.3061</td>
</tr>
<tr>
<td>0.5</td>
<td>0.519(3)</td>
<td>8.2802</td>
</tr>
<tr>
<td>0.6</td>
<td>0.602(19)</td>
<td>8.2587</td>
</tr>
<tr>
<td>0.7</td>
<td>0.692(8)</td>
<td>8.2369</td>
</tr>
<tr>
<td>0.8</td>
<td>0.792(8)</td>
<td>8.2118</td>
</tr>
<tr>
<td>0.9</td>
<td>NA</td>
<td>8.1829</td>
</tr>
<tr>
<td>0.95</td>
<td>0.935(6)</td>
<td>8.1678</td>
</tr>
<tr>
<td>0.95</td>
<td>NA</td>
<td>8.1665</td>
</tr>
<tr>
<td>1.0*</td>
<td>0.997(3)</td>
<td>8.1522</td>
</tr>
</tbody>
</table>

* Larsson et al. 1994.  

The lattice parameters were fitted by non-linear least-squares using the analyzed compositions (weighted according to their observed analytical uncertainties) to a polynomial in \( X_{Hc} \) (the molar fraction of FeAl₂O₄) to give:

\[
a_{\chi} \AA = 8.3970(1) - 0.278(11) X_{Hc} + 0.150(33) (X_{Hc})^2 - 0.116(22) (X_{Hc})^3
\]

This equation returns lattice parameters with an accuracy of ±0.0001 to ±0.0002 Å.

The reduced chi-squared for the regression is 0.53. The lattice parameters show a sinusoidal deviation from linearity (Vegard’s Law), which is expected in Fe₃O₄-containing solid solutions because of the change in site-preference of Fe²⁺ as the cation distribution in the spinel solid solution goes from basically “inverse” at Fe₂O₃ to basically “normal” at FeAl₂O₄ (O’Neill and Navrotsky 1984).

The determination of \( T_c \) across the binary system was made by using the AGICO KLY-3-CS3 \( \chi \)-Bridge (Jelinek and Pokorny 1997). The \( \chi \)-Bridge can be used in the temperature range of ~190 to 0 °C by cooling with liquid nitrogen and allowing the specimen to increase in temperature. In the range 80 to 700 °C, we used a linear heating ramp with a heating rate of 11 °C per minute for each heating cycle. The specimen is placed in a small glass tube just below the platinum resistance thermometer. The measuring vessel is heated by a platinum furnace.

To perform susceptibility measurements over a chosen temperature range, the furnace is automatically moved into and out of the pick-up coil, which produces an alternating field of 300 A/m with a frequency of 875 Hz. The measurement made out of the pick-up coil is used to automatically calibrate the measurement in the magnetic field. One potential problem with such measurements is the possible oxidation of Fe²⁺ especially for increasing hercynite concentration, and so the measurements were performed by using a dry argon atmosphere or an argon 10% hydrogen mixture pumped into the glass specimen tube.

TEM specimens were prepared by crushing under alcohol as well as ion milling. Comparison of both methods was made to avoid misinterpretation caused by specimen preparation artefacts. The TEM used for the investigations is a Jeol 3010 operating at 297 kV equipped with a LaB₆ cathode, an EDX system (Link ISIS) and a Gatan post column energy filter (GIF). The energy filter offers the possibility of yielding compositional information by allowing only those electrons, which have suffered a specific energy loss to form the image. The energy-filtered images were recorded with a slow-scan CCD camera (phosphor scintillator crystal: 1024 × 1024 pixel array) attached to the GIF. To optimize the signal to noise ratio (SNR) the experimental conditions were chosen following the recommendations of Berger and Kohl (1993). All images and spectra were gain and dark current-corrected. The energy-filtered images were recorded in the binning mode, where 2 × 2 pixels are summed into one effective pixel during the readout process, so that 512 × 512 pixel images result. To obtain element-distribution images (element maps), we removed the background contribution using the three-window method (Egerton 1996; Reimer 1995, 1997; Williams and Carter 1996). When investigating elements present only in a low concentration, the background extrapolation increases the noise content. An alternative to this method of element imaging is to calculate jump-ratio images. This method produces images with minimum added noise and is not greatly affected by many artefacts arising in elemental mapping of crystalline materials (Krivanek et al. 1993). However, these jump-ratio images are not usable for quantitative analyses. Image processing and analysis routines were written in the script language within Digital Micrograph and the quantitative analysis of the resulting spectra were performed using Gatan EL/P program packages and the software IGOR (WaveMetrics).

**RESULTS**

**Magnetic susceptibility measurements**

The inflection point of the susceptibility curve defines \( T_c \) and can be determined by the intersection of two straight lines, fitting the sharp drop and the high temperature range of the susceptibility curve (Harrison and Putnis 1999). Determining \( T_c \) for the whole range of synthetic specimens was limited by the temperature range of the \( \chi \)-Bridge and only concentrations to hercynite 80% could be measured. The measured \( T_c \) values (Fig. 1) can be fitted by a straight line, which also fits the theoretical values for hercynite and magnetite.

With increasing hercynite concentration, susceptibility curves
become non-reversible for one heating and cooling cycle and additional drops in susceptibility appear in the heating curve (Fig. 2). The first drop of the first measurement during heating gives $T_c$ for the original composition of the solid solution. Initially, we suspected these irreversible curves to be due to oxidation in the samples, but neither purging the starting materials in a dry argon atmosphere for longer periods, nor replacing the argon by an Ar/H$_2$ mixture, could modify the irreversibility of the curves.

Figure 3 shows an exemplary series of $\chi$-Bridge measurements for a sample with composition Mag$_{40}$Hec$_{60}$, where the maximum attained temperature was increased in each successive heating and cooling cycle by 20 °C, starting from 110 °C and reaching 510 °C in the final cycle. We obtained three different characteristic regions. The first range (Range I), to a maximum heating temperature of 220 °C, yields reproducible susceptibility curves for the heating and cooling runs. In the second temperature range (Range II), from 240 to 300 °C, there is a significant decrease in the maximum peak value of the $\chi$-curves for increasing maximum heating temperature, but only a slight increase in $T_c$. Characteristic for the last range (Range III) above 300 °C, is an increase of the maximum peak value of the susceptibility and additionally, a significant increase in $T_c$.

Comparison of X-ray powder diffraction measurements using a Philips X'Pert System PW3040 powder diffractometer of the quenched starting materials with samples subsequently heated in the $\chi$-Bridge showed no significant differences, despite that irreversible changes had taken place in the samples heated in both Ranges II and III.

Energy-filtered TEM results

Using conventional TEM we investigated the starting materials, and a series of compositions, which had been heated in the $\chi$-Bridge in Ranges I, II, and III. The starting materials as well as materials heated in Ranges I and II, showed no unusual contrast features or any compositional heterogeneities. Only in specimens from Range III did we find regions with a fluctuating contrast indicating some changes in structure and/or chemistry.

Given that the chemical difference in magnetite-rich or hercynite-rich regions is in the content of Fe or Al, and taking into account that the available intensity is one of the limiting factors for energy-filtered techniques, the Fe $L_2,3$-edge is the best
choice for EFTEM imaging. The white lines of the Fe $L_{2,3}$-edge are characterized by sharp maxima at the edge onset and this significantly improves the available signal and therefore the signal-to-noise. Both jump ratio images and element maps are subject to artefacts, which may be caused by variations in the specimen thickness in the former case, or by diffraction contrast in the latter. In principle, the best way to check the correctness of a result is to compare pre-edge ratio, post-edge/pre-edge jump ratio images and element maps.

Figure 4 shows such a complete series of energy-filtered images for the Fe $L_{2,3}$-edge using a sample of bulk composition $\text{Mag}_{40}\text{Hec}_{60}$ heated in the $\chi$-Bridge to 700°C. These images fulfill the criteria that the pre-edge ratio image shows no structural contrast, and the jump ratio images and elemental map have the same contrast. The Fe jump ratio images as well as the element map show oscillating Fe enrichments.

To quantify that the spatial variation of the chemical composition is sinusoidal, it is necessary to investigate a known crystallographic orientation. The magnetite–hercynite solid solution has a spinel structure and spinodal decomposition, which would be expected in this system in the early stages of unmixing, is predicted to occur in the elastically soft $<100>$ directions (Harrison and Putnis 1997), leading to three sets of mutually perpendicular modulations. At orientations normal to one modulation, the other two sets of orthogonal modulations form the so-called tweed structure (Fig. 5a), where the specimen can be tilted in the [001] zone axis. The corresponding diffraction pattern shows streaking of the diffraction spots due to the structural modulation (Fig. 5b).

By using element mapping (Figs. 4 and 6) we show the modulation of chemical composition, including the chemical gradients, and hence verify the theoretical expectation of spinodal decomposition (Cahn 1968). Under the experimental conditions in the TEM the sinusoidal chemical fluctuation is not caused by a smeared out square wave. The measured composition variation is a true reflection of the actual variation since the analysis resolution (1 nm) is much smaller than the sine wave period (16 nm). Furthermore, the specimen thickness is only approximately 47 nm therefore tilted sharp interfaces could not produce these sinusoidal chemical fluctuations. Additionally, EFTEM offers the possibility of spatially quantifying the chemical composition fluctuations. We have used the relative quantification method of Egerton (1996). We expect the chemical modulation to be equal in all three spatial directions. The thickness of the investigated specimen area can be approximately determined by using the low loss area of the electron energy loss spectrum and measuring the $t/\lambda$ ratio, where $t$ is the thickness of the investigated sample area and $\lambda$ the mean free path of inelastic scattering. For $\text{Mag}_{40}\text{Hec}_{60}$ the mean free path of inelastic scattering was calculated by using Egerton (1996) to be $\lambda = 157$ nm and for $t/\lambda = 0.3$ a specimen thickness of approximately 47 nm was obtained. Since the wavelength of the modulation in the plane of the specimen is approximately 16 nm, this thickness represents 3 complete modulations. We can now use a linescan to determine quantitatively the chemical oscillation, which automatically integrates the chemical composition through the thickness.

The spatially resolved Fe/O ratio can be quantified by mapping the Fe and O concentration shown in Figures 6b and 6c and using the experimentally determined k-factors of Golla and Putnis (2001) to calculate the Fe/O distribution image shown in

![Figure 4](image4.png)  
 Figure 4. Series of energy-filtered images of the Fe $L_{2,3}$-edge, zone axis [530]. (a) First pre-edge image. (b) Second pre-edge image. (c) Post-edge image. (d) Ratio of the pre-edge images. (e) The Fe element map and (f) the Fe jump-ratio image.

![Figure 5](image5.png)  
 Figure 5. CTEM image and corresponding diffraction pattern, zone axis [001]. (a) Tweed structure produced by structural modulation and (b) corresponding diffraction pattern. The corresponding diffraction image verifies this modulation by showing streaking of the diffraction spots due to the structural modulation.
Additionally we can now calculate the concentration modulation in terms of the magnetite and hercynite solid solution, which is shown in the line scan of Figure 6e.

To verify that the domains of compositional fluctuations are coherent, we have taken HRTEM images of the same specimen area as used for the chemical investigation. One example of such an image is shown in Figure 7a, which is free of dislocations. Figure 7b shows a magnified part of this image with an inset (7c) of a theoretically calculated high resolution TEM image using the JEMS software package (Stadelmann 1987). The simulation and experimentally taken HRTEM images yield a good agreement. The contrast modulation in the HRTEM images can be due to local thickness differences or to some contribution from the diffraction contrast.

**DISCUSSION**

Measurements of the susceptibility-temperatures curves for a series of solid solution compositions across the magnetite-hercynite join shows a linear correlation between the Curie temperature and the magnetite concentration in the solid solution. Although the magnetic transition temperature for hercynite-rich compositions could not be reached, the linear trend fits the theoretical Curie temperature for the end-members. The susceptibility curves show no anomalies, which would indicate compositional heterogeneities.

Heating the samples to 220 °C and cooling produces no irreversible changes in the susceptibility curves, and therefore presumably no changes in the structure of the solid solution. However, heating at temperatures in Range II, above 220 °C, results in progressive irreversible changes which become more pronounced the higher the heating temperature. The changes are characterized by progressive reductions in the susceptibility, but no signs of compositional heterogeneities, which would be indicated by variable Curie temperatures within the sample. There is no evidence for oxidation, either by HRTEM or by the presence of maghemite-like magnetic susceptibility signatures. At no stage in any of the experiments was maghemite detected, even in those samples heated to 700 °C (maghemite has a Curie temperature of 645 °C). Although the formation of point defects due to Fe²⁺ → Fe³⁺ oxidation cannot be entirely discounted, it is thought unlikely in the experimental circumstances.

A more reasonable conclusion for the Range II behavior is some relaxation of the Fe²⁺/Fe³⁺ ordering from the quenched state towards a more equilibrium distribution. Magnetite is an inverse spinel, and hercynite is normal, although the distribution of ions among the octahedral and tetrahedral sites in the quenched samples is not known. However, whatever assumptions are made about this state of disorder, any tendency to order the solid solution either towards an inverse or a normal cation distribution, will result in a reduction in magnetization and susceptibility. This can be readily demonstrated for an intermediate composition Mag₅₀Hec₅₀ (Fe²⁺Fe³⁺AlO₄) in which both an ordered inverse distribution (Fe³⁺ on tetrahedral sites, Fe²⁺ and Al on octahedral sites) or a normal distribution (Fe²⁺ on tetrahedral sites, Fe³⁺ and Al on octahedral sites) have a saturation magnetization of 1 μ₀, whereas a completely disordered distribution (1/3 Fe²⁺, 1/3 Fe³⁺ on tetrahedral sites, 2/3 Fe²⁺, 2/3 Fe³⁺ on octahedral sites) would have a saturation magnetization of 3 μ₀. A partially ordered state in which the Al occupies half of the octahedral sites, with the rest of the octahedral and tetrahedral sites equally occupied by Fe²⁺ and Fe³⁺ would have a zero magnetization.

The behavior of the magnetic susceptibility curves in Range III

**FIGURE 6.** (a) CTEM image of spinodal decomposition of Mag₅₀Hec₅₀, (b, c) element map of Fe and O, respectively (d) ratio image of the Fe/O element map and (e) corresponding line scan of d with the calculated concentration modulation of magnetite and hercynite.
is consistent with an irreversible change in the homogeneity of the sample, with regions of higher $T_c$ (i.e., more magnetite-rich). The TEM observations are unequivocal and show contrast variations throughout all samples with average hercynite component above 30%, and heated in this range. A detailed EFTEM and HRTEM study of a sample of composition $\text{Mg}_6\text{Hec}_4\text{Fe}_2\text{O}_8$ heated to 700 °C confirmed that the periodic contrast variations were due to sinusoidal compositional modulations with a wavelength of 16 nm. The peak and trough compositions in the modulation differed by approximately 15 mol%. The HRTEM images show that the modulations are coherent.

The sinusoidal nature of the modulations and the absence of dislocations demonstrate that the exsolution is spinodal decomposition. Although this mechanism might well be expected in this system, this is the first report, to the authors’ knowledge, of an experimentally measured sinusoidal fluctuation in composition on such a small scale, and demonstrates the power of EFTEM for such high-resolution analysis.

ACKNOWLEDGMENTS

We thank Richard Harrison for help with the software code used to analyze the susceptibility curves. This work was supported by the Deutsche Forschungsgemeinschaft (DFG), grant Pu 153/2-2.

REFERENCES CITED


 References