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The effect of oxidation and reduction on thermal expansion of magnetite from 298 to 1173 K at different vacuum conditions

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Abstract

Three thermal expansion curves of natural and synthetic magnetite (Fe_3O_4) have been measured under different vacuum conditions (10^{-4} and 10^{-6} mbar). The different behavior in thermal expansion depends on vacuum level, which controls the partial oxidation of the sample. If the vacuum is poor, that is in mildly oxidizing conditions, the thermal expansion curve presents a discontinuity at 875 K and the samples oxidizes. In non-oxidizing conditions the discontinuity is not present and the thermal expansion coefficient is markedly smaller. The experimental curves indicate that virtually all thermal expansion data on magnetite in the literature were measured on oxidized or partially oxidized samples.

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1. Introduction

Magnetite, ideally $Fe^{II}Fe_2^{III}O_4$, is a mineral phase with the spinel structure, described by a cubic close packing of oxygen atoms with a half of the octahedral and one-eighth of the tetrahedral cavities occupied by the Fe cations (see for example [1]). 'Normal' spinels have divalent cations in tetrahedral coordination and trivalent cations in octahedral coordination, whereas 'inverted' spinels such as magnetite have half of the Fe^{3+} and the Fe^{2+} cations in four-fold coordination, while the remaining Fe^{3+} cations statistically occupy the octahedral site. These two configurations are related by a continuous order–disorder transition, as in many other spinel compositional systems.

Magnetite is one of the better studied spinels because of its magnetic proprieties, but to date only limited work has been performed on its thermal expansion properties at high temperature ([2,3], and more recently [4]). Sharma [2] performed two interferometric measurements in the T ranges 326–764 and 735–985 K. Measurement of lattice parameters by X-ray single crystal diffraction was used by Gorton et al. [3] and Okudera et al. [4] up to 1273 and 773 K, respectively. All the cited experiments have been performed in air and no control on the sample oxidation was possible, due to the intrinsic characteristics of the techniques applied by the authors, which do not allow the detection of newly formed maghemite or hematite, neither during nor after the heating. In their work, both Sharma and Gorton highlighted a discontinuity in the cell parameters around 850 K, very close to the Curie temperature, that could be related to the magnetic transition. Okudera, on the other side, did not reach the Curie temperature, so he reports only a slight thermal expansion change, explained by cation reordering on heating. All these hypotheses do not take into account the possibility of an oxidation of the Fe^{II} that cannot be neglected if magnetite is heated in oxidizing conditions.

In this work, we observe that in magnetite the measured lattice constants and the derived thermal expansion coefficients, including the discontinuities, are strongly dependent on the experiment oxidizing–reducing atmosphere.

2. Experimental

We have performed thermal runs using two different vacuum conditions (run1 $P = 10^{-4}$ mbar and run2 $P = 10^{-6}$ mbar) on a well-characterized natural sample.

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The magnetite sample from Cogne (Aosta, Western Alps) has been purified from phyllosilicate phases using magnetic and heavy liquid separation. The cell-edge parameter has been determined by means of X-ray powder diffraction to be $a = 8.3950(1)$ Å. This value is in good agreement with the parameter determined by Gorton et al. [3] and Fleet [5] and there is no indication for this sample to have an inversion degree different from the one of a synthetic magnetite. An additional measurement (run3) has been collected on a synthetic sample (Aldrich 51,815-8) using the same experimental conditions as in run1.

The thermal expansion data were collected by X-ray powder diffraction using a Siemens D-500 diffractometer equipped with a Bühler HTK1400 high-temperature chamber. Vacuum conditions were obtained by means of a diffusive oil pump to 10^{-4} mbar and a turbomolecular pump to 10^{-6} mbar. The chamber pressure was measured by means of a gauge close to chamber outlet, so that they represent the highest possible air pressure on the sample. Two different X-ray tube anodes have been used: cobalt ($K_{\alpha 1\mathrm{Co}} = 1.78897$ Å) in run1, and copper ($K_{\alpha 1\mathrm{Cu}} = 1.54056$ Å) in run2 and run3. The magnetite sample was heated by a platinum–rhodium strip, which is, at the same time, the sample holder and the heater. A very thin layer of powder sample was employed to avoid thermal gradients within the sample. The temperature was measured by a Pt–Rh thermocouple attached to the metal strip. Although the small sample thickness produces transparency effect, the resulting variations in the peak intensities do not affect the peak position and the refined lattice parameters relevant to this work. The thermal expansion of the metal strip could instead affect the sample position during heating, so that the use of an internal standard was required, in order to achieve at the same time good temperature and peak position calibration.

All powder data sets were collected in the angular range 25–140°2ϑ, using steps of 0.02°2ϑ and counting time 6 s/step. Standard silicon (NIST SRM 640b) has been used as internal standard to correct for the zero shift and sample displacement. The Si thermal expansion model [6] has been used to calculate the silicon lattice parameters at high temperature.

The powder diffraction patterns were analyzed by the full-profile Rietveld method using the GSAS software [7]. The background was modeled by a 10-terms cosine polynomial function, and the peak profiles were described by a pseudo-Voigt function. The refinement strategy was as follows: (i) the silicon lattice parameters were fixed at each nominal temperature at the theoretical values; (ii) the instrumental parameters (zero-shift, sample displacement, and peak profile parameters including asymmetry) were refined on the basis of the Si lattice constants assuming that the estimation of the temperature is correct within 5 K; (iii) the lattice parameters and peak profile parameters of magnetite were finally refined.

The use of the internal standard and the adopted refinement strategy allowed internal consistency of the data and intrinsic correction for the displacement effects of the sample-holder because of the thermal distortion.

3. Discussion of the results and conclusions

The fitted profile diffractograms reported in Fig. 1 refer to the natural magnetite with two different conditions of partial oxygen pressure at 1073 K (run1), 1073 K (run2) and 973 K (run3). In run1 and run3 the presence of hematite can be easily detected, moreover in the last run there are two extra peaks that are attributed to maghemite (formally γ-Fe$_3$O$_4$) that is the iron-defective phase of magnetite. This is a clear indication that oxidation has taken place during the experiment. On the contrary, in the powder patterns of run2, only magnetite and silicon are present, showing no extra peak due to newly formed phases. The different oxidation conditions on the sample have a marked effect on the measured thermal expansion. In fact, as highlighted in Fig. 2, the lattice parameter variations as a function of temperature for the oxidized samples are substantially larger than for not-oxidized sample, as expected. Moreover, while for run1 and run3 a distinguished slope change can be observed at about 873 K, in run3 the cell parameter expands smoothly with temperature, with no slope changes. The local derivatives of thermal expansions are shown in Fig. 3, where the different thermal behaviors of the lattice parameters under different oxidizing conditions can be readily appreciated.

The thermal expansion coefficients have been extracted using the following equation [8]:

$$\ln\frac{V(T)}{V_{T_\mathrm{r}}} = a_0 T + \frac{1}{2}a_1 T^2 - A$$

$$A = a_0 T_\mathrm{r} + \frac{1}{2}a_1 T_\mathrm{r}^2,$$

where $V(T)$ is the cell volume at temperature T, V_{T_r} is the cell volume at the reference temperature ($T_\mathrm{r} = 298$ K). The three expansion curves have been fitted by a second-order polynomial. The curves relative to the oxidized sample have been split in two parts, below and above the slope change (T_a). The measured thermal expansion coefficients (a_0 and a_1) are reported in Table 1.

The high quality of the present results can be appreciated if the data are compared to the previously reported thermal expansion data on magnetite. In Fig. 4, the thermal expansion curves reported by Gorton et al. [3] and Okudera et al. [4] are plotted together with our data for comparison. It can be seen that literature data are perfectly comparable to our results from run1,

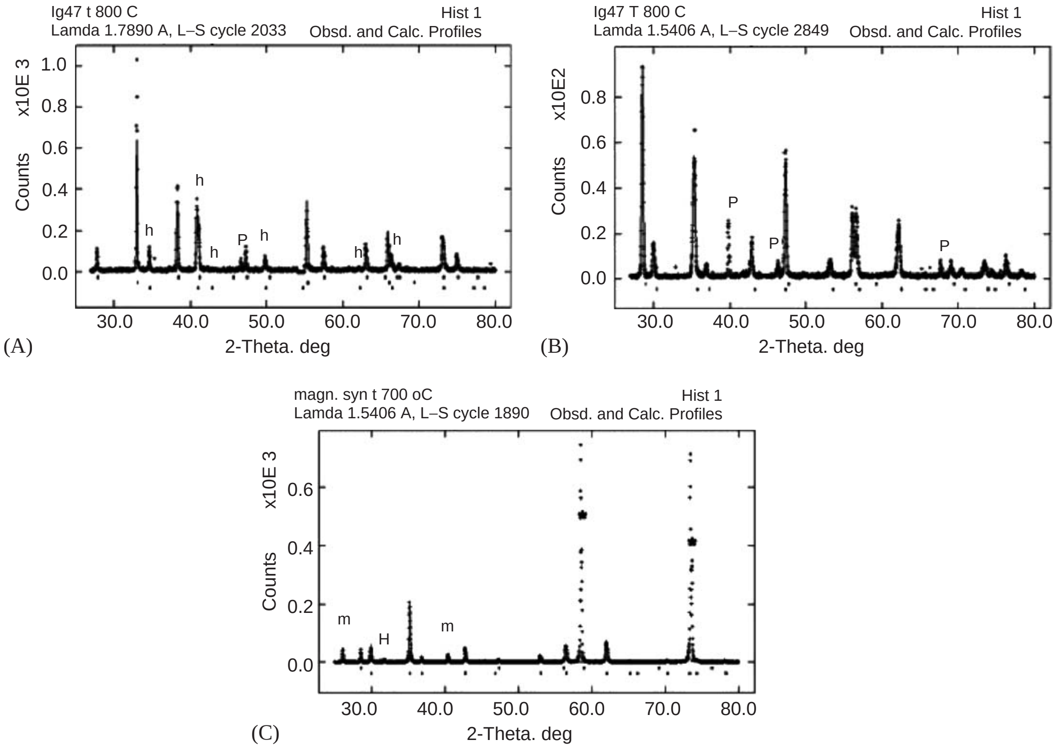

Fig. 1. (A) Diffraction pattern of magnetite at 800°C in run1 (h = hematite p = sample holder), (B) diffraction pattern of magnetite at 800°C in run2 (p = sample holders), and (C) diffraction pattern of magnetite at 700°C in run3 (m = maghemite, h = hematite, * = sample holder).

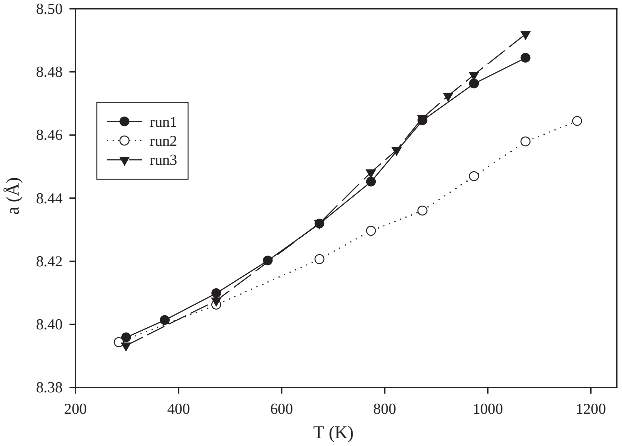

Fig. 2. Thermal expansion of the cell edge of magnetite as a function of temperature for the different runs. The error bars are smaller than the symbols.

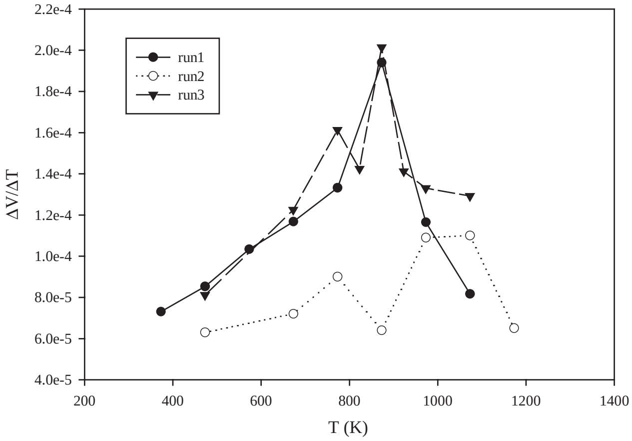

Fig. 3. The local derivatives of the thermal expansion curves.

where oxidation occurs. Of course, this is a clear indication that all reported data for the thermal expansion of magnetite in the literature are also affected by oxidation. As previously mentioned, because of the experimental methods adopted (interferometry and single crystal X-ray diffraction) neither [2,3] or [4] could properly assess the degree of oxidation of the sample.

The presence of maghemite in run3 suggests that the expansion of the cell edge in magnetite is due to an increase of iron defects in the structure. Below 800 K these defects are not sufficiently concentrated to give a symmetry change (magnetite–maghemite), but are sufficient to produce a macroscopic difference between oxidized (run1) and 'normal' (run2) thermal expansions.

Unfortunately, the data quality of our measurements, performed in order to obtain precise cell variations with temperature, was not ideal to carry out a multiphase analysis or even a quantitative investigation of the oxidation kinetics.

Table 1
Calculated thermal expansion coefficients

	T_a (°C)	$T < T_a$		$T > T_a$	
		a_0 (10^{-6}) (K^{-1})	a_1 (10^{-8}) (K^{-2})	a_0 (10^{-6}) (K^{-1})	a_1 (10^{-8}) (K^{-2})
Run1	550	7.5(4)	2.76(4)	155.3[a]	−6.180[a]
Run2	550	13.0(3)	1.2(3)	114.3(7)	−3.0(2)
Run3	550	1.4(4)	3.7(4)	77.(6)	−1.6(3)

[a] Calculated on 3 points.

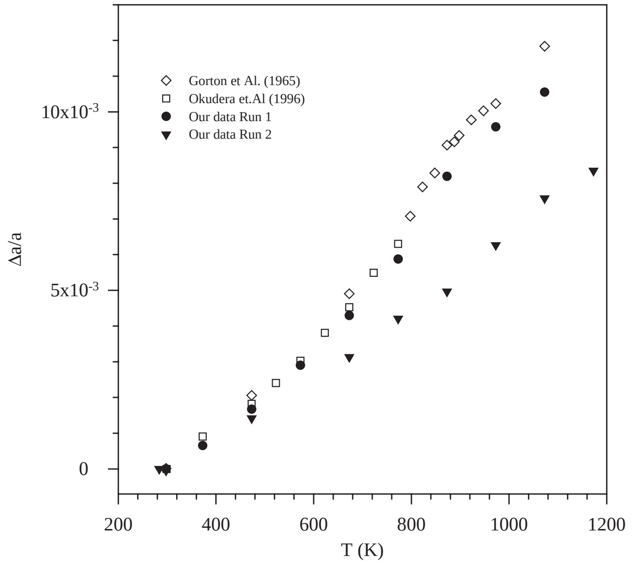

Fig. 4. Comparison of the thermal expansion curves of run1 and run2 with the two more recent data sets from the literature.

Following these results, the common interpretation of the slope change at about 850 K has to be reformulated. In fact, this change needs to be related to the oxidation of magnetite, via the defective spinel structure maghemite that subsequently partially transforms into hematite.

The previously reported values for the thermal expansion of magnetite are not to be considered correct, due to partial sample oxidation. The correct values can be extracted from the results in the data set from run2, in which the thermal expansion was measured at high temperature with no detectable oxidation of the original magnetite sample.

Acknowledgments

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