



Reduced partition function ratios of iron and oxygen in goethite

M. Blanchard^{a,*}, N. Dauphas^b, M.Y. Hu^c, M. Roskosz^d, E.E. Alp^c,
D.C. Golden^e, C.K. Sio^b, F.L.H. Tissot^b, J. Zhao^c, L. Gao^c, R.V. Morris^f,
M. Fornace^b, A. Floris^g, M. Lazzeri^a, E. Balan^a

^a Institut de Minéralogie, de Physique des Matériaux, et de Cosmochimie (IMPMC), Sorbonne Universités – UPMC Univ Paris 06, UMR CNRS 7590, Muséum National d'Histoire Naturelle, IRD UMR 206, 4 Place Jussieu, F-75005 Paris, France

^b Origins Laboratory, Department of the Geophysical Sciences and Enrico Fermi Institute, The University of Chicago, 5734 South Ellis Avenue, Chicago, IL 60637, USA

^c Advanced Photon Source, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, USA

^d Unité Matériaux et Transformations, Université Lille 1, CNRS UMR 8207, 59655 Villeneuve d'Ascq, France

^e Engineering and Science Contract Group-Hamilton Sundstrand, Mail Code JE23, Houston, TX 77058, USA

^f NASA Johnson Space Center, Houston, TX, USA

^g Department of Physics, King's College London, Strand, London WC2R 2LS, United Kingdom

Received 25 June 2014; accepted in revised form 4 December 2014; available online 16 December 2014

Abstract

First-principles calculations based on the density functional theory (DFT) with or without the addition of a Hubbard U correction, are performed on goethite in order to determine the iron and oxygen reduced partition function ratios (β -factors). The calculated iron phonon density of states (pDOS), force constant and β -factor are compared with reevaluated experimental β -factors obtained from Nuclear Resonant Inelastic X-ray Scattering (NRIXS) measurements. The reappraisal of old experimental data is motivated by the erroneous previous interpretation of the low- and high-energy ends of the NRIXS spectrum of goethite and jarosite samples (Dauphas et al., 2012). Here the NRIXS data are analyzed using the SciPhon software that corrects for non-constant baseline. New NRIXS measurements also demonstrate the reproducibility of the results. Unlike for hematite and pyrite, a significant discrepancy remains between DFT, NRIXS and the existing Mössbauer-derived data. Calculations suggest a slight overestimation of the NRIXS signal possibly related to the baseline definition. The intrinsic features of the samples studied by NRIXS and Mössbauer spectroscopy may also contribute to the discrepancy (e.g., internal structural and/or chemical defects, microstructure, surface contribution). As for oxygen, DFT results indicate that goethite and hematite have similar β -factors, which suggests almost no fractionation between the two minerals at equilibrium.

© 2014 Elsevier Ltd. All rights reserved.

1. INTRODUCTION

For decades now, the isotopic compositions of natural samples have been measured and found countless applications in all branches of geosciences (see for reviews,

Valley and Cole, 2001; Johnson et al., 2004; Eiler et al., 2014). In the meantime, isotope exchange experiments were performed to improve our understanding of the processes responsible for stable isotope fractionation. More recently, new approaches have emerged and are contributing to this field of research. First-principles calculations give reduced partition function ratios (also called β -factors) that can be combined for two phases in order to obtain the equilibrium isotope fractionation factor (α -factor), which is the quantity

* Corresponding author. Tel.: +33 1 44 27 98 22; fax: +33 1 44 27 37 85.

E-mail address: marc.blanchard@impmc.upmc.fr (M. Blanchard).

usually measured. These theoretical methods are also of great interest for investigating the mechanisms controlling the isotope fractionation at the molecular scale. For Mössbauer active elements (like iron), β -factors can also be obtained using Mössbauer spectroscopy through the measurement of the temperature dependence of the isomer shift (Polyakov and Mineev, 2000) or using Nuclear Resonant Inelastic X-ray Scattering (NRIXS, Polyakov et al., 2005, 2007; Dauphas et al., 2012, 2014).

Dauphas et al. (2012) and Hu et al. (2013) reported NRIXS data for ^{57}Fe -rich goethite $\text{FeO}(\text{OH})$, hydronium-jarosite $(\text{H}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$ and potassium jarosite $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$. From such measurements, one can deduce iron β -factors as a function of temperature. Polyakov et al. (2007) had used projected partial phonon density of states (pDOS) obtained using this technique to calculate β -factors for various phases. Dauphas et al. (2012) and Hu et al. (2013) used a different approach based on moment estimates of NRIXS scattering spectrum $S(E)$, which simplifies evaluation of measurement uncertainties and potential systematic errors. The study of Dauphas et al. (2012) was the first of its kind in measuring NRIXS spectra specifically for applications to isotope geochemistry. In doing so, they encountered a difficulty that had been unappreciated before concerning the baseline at low and high energies. Most previous studies in geosciences had focused on estimating the Debye sound velocity (Hu et al., 2003; Sturhahn and Jackson, 2007), from which compressional and shear wave velocities can be deduced if the bulk modulus and density of the phase are known. These estimates are derived from parts of the spectra that are close to the elastic peak for the nuclear transition of ^{57}Fe at 14.4125 keV. On the other hand, the force constant, which controls β -factors, is heavily influenced by details of the spectrum at the low- and high-energy ends of the spectrum. As a result, little attention had been paid to the accuracy of force constant measurements by NRIXS. Dauphas et al. (2012) found that in some cases, significant counts were present even at high energies. The projected partial phonon density of states, $g(E)$, and the scattering spectrum, $S(E)$, never reached zero and as a result, the integrals that gave the force constants did not plateau for goethite and H-jarosite. These were interpreted to reflect the presence of multiple phonons at high energies. However, we were unable to replicate the measurements during another session of NRIXS measurements at the Advanced Photon Source synchrotron. This and other tests performed on other phases convinced us that the high counts in the tails are not from multiple phonons but rather reflect the presence of a non-constant baseline. To address this issue, Dauphas and collaborators have developed a software (SciPhon) that reliably corrects for non-constant baseline (Dauphas et al., 2014).

In the present study, the pDOS as well as the iron and oxygen β -factors of goethite are computed using first-principles calculations and compared to available experimental isotopic data. In parallel, the data published in Dauphas et al. (2012) have been re-evaluated using SciPhon and we present revised estimates for the force constants of goethite and jarosite. To validate the approach and evaluate the

long-term reproducibility of force constant measurements by NRIXS, we have analyzed the goethite sample two more times and the jarosite samples one more time. Those new results, together with a re-evaluation of previous data, are reported here.

2. MATERIALS AND METHODS

2.1. NRIXS spectroscopy

Nuclear Resonant Inelastic X-ray Scattering is a nuclear spectroscopic technique that uses the nuclear transition of ^{57}Fe at 14.4125 keV to probe the vibration properties of iron (Seto et al., 1995; Sturhahn et al., 1995). The method as implemented at sector 3-ID-B of the Advanced Photon Source at Argonne National Laboratory is briefly described hereafter. The incident beam is a pulsed X-ray beam of 70 ps duration and 153 ns interpulse duration. A monochromator restricts the energy spread of the incident beam to 1 meV. When the pulse hits the sample, X-rays are scattered by electrons and this electronic contribution is almost instantaneous. On the other hand, the excited ^{57}Fe nuclei have a finite lifetime of 141 ns and the electronic contribution can be eliminated from the signal by applying some time discrimination. The signal from NRIXS is measured using Avalanche Photodiodes (APD). The energy is scanned around the nominal resonant energy over a typical interval of -150 to $+150$ meV. When the photon energy is higher than the resonance energy, the excess energy can be lost to excitation of phonon modes in the lattice and the nuclear excitation can still occur (phonon creation). When the energy is lower than the nominal resonance energy, the energy deficit can be provided by lattice vibrations and the nuclear excitation can still occur (phonon annihilation).

From NRIXS spectra one can calculate β -factors by taking the moments of the scattering spectrum $S(E)$ (Dauphas et al., 2012; Hu et al., 2013) or the projected partial phonon density of states $g(E)$ (Polyakov et al., 2005; Dauphas et al., 2012). In the present study, all samples were fine powders (isotropic) and the calculated pDOS represents an average from contributions of all crystallographic orientations. The pDOS is partial in the sense that NRIXS is only sensitive to ^{57}Fe . Using $S(E)$, the formula that gives β -factors is (Dauphas et al., 2012),

$$1000 \ln \beta \approx 1000 \left(\frac{M}{M^*} - 1 \right) \frac{1}{E_R} \left[\frac{R_3^S}{8k^2 T^2} - \frac{R_5^S - 10R_2^S R_3^S}{480k^4 T^4} + \frac{R_7^S + 210(R_2^S)^2 R_3^S - 35R_3^S R_4^S - 21R_2^S R_5^S}{20160k^6 T^6} \right], \quad (1)$$

where M and M^* are the masses of the two isotopes considered (e.g., 56 and 54), E_R is the free recoil energy (1.956 meV for ^{57}Fe), k is Boltzmann's constant, T is the temperature, and R_i^S is the i th centered moment of S given by $R_i^S = \int_{-\infty}^{+\infty} S(E)(E - E_R)^i dE$. Eq. (1) was derived by Dauphas et al. (2012) and Hu et al. (2013) using two different mathematical approaches (expansions in powers of temperature *vs.* thermalized moments).

Download English Version:

<https://daneshyari.com/en/article/4701906>

Download Persian Version:

<https://daneshyari.com/article/4701906>

[Daneshyari.com](https://daneshyari.com)