

# Infrared- and Raman-Active Phonons of Magnetite, Maghemite, and Hematite: A Computer Simulation and Spectroscopic Study

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Magnetite, maghemite, and hematite have been the subject of numerous studies using vibration spectroscopy to determine their infrared- and Raman-active phonons. However, no complete and unambiguous set of experimentally observed optically active phonons has yet been reported for these iron oxides. The use of atomistic simulation methods with a transferable Buckingham potential provides new data for the phonon densities of states of magnetite and the two associated phases, hematite and maghemite.

## 1. Introduction

The unusual properties of magnetite have spurred a continued effort toward elucidating the processes of its formation as a passive film,<sup>1</sup> the occurrence of magnetite on earth and planetary surfaces,<sup>2</sup> and the nature of the Verwey transition at 120 K.<sup>3</sup>

Central to most of these studies is the use of vibration spectroscopy to determine the phonon density of states. There have been numerous studies of the vibration spectra of magnetite, with the majority employing infrared absorption and Raman scattering<sup>4–9</sup> to assign the four  $T_{1u}$  infrared-active phonons and the  $A_{1g}$ ,  $E_g$ , and  $3T_{2g}$  Raman-active modes, respectively.

There is some confusion over the assignments of the phonons for magnetite, particularly the Raman-active phonons. De Faria et al. have shown<sup>9</sup> that laser power is an important consideration when interpreting Raman data. Heating or moderate laser power converts magnetite to hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) and maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>), and some of the earlier Raman data shows evidence of attributing phonons of hematite or maghemite impurity to the parent magnetite phase. A recent study<sup>10</sup> of the effects of laser-induced thermal effects on magnetite has confirmed the findings of de Faria et al.

Absence of a complete and unambiguous set of observed optically active phonons has led us to use atomistic simulation methods to obtain the phonon density of states for magnetite and the two associated phases, hematite and maghemite.

## 2. Atomistic Simulation

The simulation techniques have been described comprehensively elsewhere<sup>11–14</sup> and have been previously applied to a range of mixed metal oxides.<sup>15–19</sup> The calculations were carried out using energy minimization procedures embodied in the GULP code. The interatomic potentials are based on the Born model of the solid, which includes a long-range Coulombic

interaction and a short-range term to model overlap repulsions and van der Waals forces

$$V_{ij}(r_{ij}) = [-Z_i Z_j e^2 / r] + [A_{ij} \exp(-r/\rho_{ij}) - C/r_{ij}^6] \quad (1)$$

The electronic polarizability of the ions is described by the shell model, which is effective in simulating the dielectric and lattice dynamical properties of metal oxides. It should be stressed that employing such a potential model does not necessarily mean that the electron distribution corresponds to a fully ionic system and that the validity of the potential model is assessed primarily by its ability to reproduce observed crystal properties. In practice, it is found that models based on formal charges work well even for compounds such as silicates and zeolites in which there is a significant degree of covalency.

The simulations of the iron oxide lattices were performed using two-body potentials for Fe<sup>3+</sup>–O, Fe<sup>2+</sup>–O, and O<sup>2–</sup>–O<sup>2–</sup> interatomic interactions that have been developed by Catlow et al.<sup>20–22</sup> The shell model parameters interactions were refined to achieve the best fit of the predicted wavenumbers of infrared- and Raman-active vibrations to experimentally observed wavenumbers. The short-range potential parameters for each ion–ion interaction and shell model parameters for Fe<sub>3</sub>O<sub>4</sub>,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> used in this study are listed in Tables 1, 4, and 7. The calculated lattice parameters and atomic positions after energy minimization to generate a relaxed equilibrium structure for studied iron oxides are reported in Tables 2, 5, and 8. The data show excellent agreement with the experimentally observed structures.

The phonon calculations presented here are based on standard methodology involving the Cartesian second derivative matrix. The vibrational frequencies are the square roots of the eigenvalues of the dynamical matrix, which consists of the mass-weighted second derivatives. Such methods have been used<sup>23–25</sup> to calculate the phonon dispersion curves of oxides, such as  $\alpha$ -SiO<sub>2</sub>, UO<sub>2</sub>, and La<sub>2</sub>CuO<sub>4</sub>, and to interpret the vibrational spectra of the important class of proton insertion materials based on  $\lambda$ -LiMn<sub>2</sub>O<sub>4</sub>.<sup>26</sup>

## 3. Discussion

**3.1. The Infrared- and Raman-Active Phonons for Magnetite.** Gasparov et al.<sup>3</sup> provide the most complete infrared and

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**TABLE 1: Interatomic Potentials for Magnetite**

Short Range			
interaction	<i>A</i> (eV)	$\rho$ (Å)	<i>C</i> (eV Å <sup>6</sup> )
Fe <sup>3+</sup> ...O <sup>2-</sup>	1102.4	0.3299	0
Fe <sup>2+</sup> ...O <sup>2-</sup>	694.1	0.3399	0
Fe <sup>3+</sup> ...O <sup>2-</sup>	1102.4	0.3299	0
O <sup>2-</sup> ...O <sup>2-</sup>	22764	0.149	15
Shell Model			
	<i>Y</i> (e)	<i>k</i> (eV Å <sup>-2</sup> )	
Fe <sup>3+</sup>	4.97	304.7	
Fe <sup>2+</sup>	2	10.92	
O <sup>2-</sup>	-2.239	60	

**TABLE 2: Calculated and Experimental Crystal Properties for Magnetite**

Unit Cell Parameters		
<i>a</i> (exp) Å	<i>a</i> (calcd) Å	
8.39	8.41	
Atomic Coordinates <i>Fd3m</i>		
species	xyz (exp)	xyz (calcd)
Fe <sup>2+</sup> Fe <sup>3+</sup> (16d)	0.625	0.625
Fe <sup>3+</sup> (8a)	0.375	0.381
O <sup>2-</sup> (32e)	0	0

**TABLE 3: Calculated and Observed Wavenumbers for Magnetite with Intensity of Infrared-Active Phonons Shown in Parentheses**

obs <sup>3</sup> /cm <sup>-1</sup>	calcd/cm <sup>-1</sup>	sym species	activity	ions involved
210	231(0.05)	T <sub>1u</sub> (1)	IR	A, B, O
193	241	T <sub>2g</sub> (1)	Raman	A, O
308	296	T <sub>2g</sub> (2)	Raman	O
270	326(2.0)	T <sub>1u</sub> (2)	IR	A, B, O
350	360(0.06)	T <sub>1u</sub> (3)	IR	A, B, O
	505	E <sub>1g</sub>	Raman	B, O
540	581	T <sub>2g</sub> (3)	Raman	A, O
560	491(0.6)	T <sub>1u</sub> (4)	IR	A, B, O
670	666	A <sub>1g</sub>	Raman	O

Raman measurements of magnetite in a study of the metal-insulator and structural transition (Verwey transition) at 120 K. Their temperature-dependent infrared and Raman data enable phonons attributable to the low-temperature orthorhombic insulator phase to be separated from those of the high-temperature spinel phase. They report polarized Raman spectra with the polarizations of the incident and scattered light parallel and perpendicular that discriminate clearly between the A<sub>1g</sub> and the three T<sub>2g</sub> modes. However, they do not observe the Raman-active E<sub>g</sub> mode. Verbe assigned a 420 cm<sup>-1</sup> band measured at 77 K as E<sub>g</sub>, but it is more likely attributable to a band of the low-temperature orthorhombic phase. The infrared data of Gasparov et al. confirms earlier assignments for the two most intense infrared-active T<sub>1u</sub> modes but does not identify the remaining two T<sub>1u</sub> modes.

The phonon calculations for magnetite are based on the potential given in Table 1 that reproduces the cell parameters satisfactorily. The phonon calculations based on this potential are compared with the data of Gasparov et al. in Table 3. Agreement is generally satisfactory, confirming the assignments of Gasparov et al. for the A<sub>1g</sub> and three T<sub>2g</sub> modes and therefore giving some confidence in the calculated E<sub>g</sub> phonon at 505 cm<sup>-1</sup>.

There is also satisfactory agreement between the observed and calculated data for the infrared-active T<sub>1u</sub> modes. The lowest wavenumber mode is calculated to be at 231 cm<sup>-1</sup>, a value well above the assignment of Degiorgi et al., a result that supports the conclusion of Gasparov et al. that the two lowest wave-

**TABLE 4: Interatomic Potentials for Maghemite**

Short Range			
interaction	<i>A</i> (eV)	$\rho$ (Å)	<i>C</i> (eV Å <sup>6</sup> )
Fe <sup>3+</sup> ...O <sup>2-</sup>	1102.4	0.329	0
Fe <sup>2+</sup> ...O <sup>2-</sup>	694.1	0.340	0
Fe <sup>3+</sup> ...O <sup>2-</sup>	1102.4	0.329	0
O <sup>2-</sup> ...O <sup>2-</sup>	22764	0.143	43
Shell Model			
	<i>Y</i> (e)	<i>k</i> (eV Å <sup>-2</sup> )	
Fe <sup>3+</sup>	4.97	805	
Fe <sup>2+</sup>	2	301	
O <sup>2-</sup>	-2.239	60	

**TABLE 5: Calculated and Experimental Crystal Properties for Maghemite**

Unit Cell Parameters		
<i>a</i> (exp) Å	<i>a</i> (calcd) Å	
8.351	8.455	
Atomic Coordinates <i>Pm3m</i>		
species	xyz (exp)	xyz (calcd)
Fe <sup>3+</sup>	0.125	0.125
	0.366	0.374
	-0.116	0.875
Fe <sup>3+</sup>	0.625	0.625
	0.625	0.625
	0.625	0.625
Fe <sup>2+</sup>	1.0	0.99
	1.0	0.99
	1.0	0.99
O <sup>2-</sup>	0.386	0.391
	0.386	0.391
O <sup>2-</sup>	0.117	0.108
	0.13	0.108
	0.383	0.391

number T<sub>1u</sub> modes observed by Degiorgi et al. are due to phonons of the orthorhombic phase.

There is a weak band observed in the 300 K optical conductivity data of Gasparov et al. that matches the calculated infrared-active phonon at 231 cm<sup>-1</sup>, with a very small calculated intensity.

The two most intense T<sub>1u</sub> modes observed at 350 and 560 cm<sup>-1</sup> can be matched with the phonons calculated at 326 and 491 cm<sup>-1</sup> with relative intensities of 2.1 and 0.6. The weak T<sub>1u</sub> mode at 360 cm<sup>-1</sup> would not be resolvable at temperatures above the Verwey transition and forms a part of the envelope of T<sub>1u</sub>(2). Variation in the published infrared peak positions is probably due to this weak unresolved T<sub>1u</sub> mode.

**3.2. The Infrared- and Raman-Active Phonons for Maghemite.** The magnetite Buckingham potential was used with the *A* and  $\rho$  parameters unchanged but with an increase in the oxygen *C* parameter. The shell model spring constants for Fe<sup>3+</sup>, Fe<sup>2+</sup>, and O<sup>2-</sup> were adjusted, but the charges on the three ions were held at the values found for magnetite. The potential shown in Table 4 reproduces the *a* cell parameter for maghemite (Table 5) within less than 0.5%.

The more complex unit cell of maghemite compared with magnetite results in many more Raman- and infrared-active phonons. The observed and calculated phonon data are shown in Table 6. The inverse spinel lattice of maghemite is observed to be iron-deficient, and this results in observed infrared and Raman spectra that are dependent on the method of sample preparation. De Faria et al.<sup>9</sup> report three broad bands in the

**TABLE 6: Calculated and Observed Wavenumbers for Maghemite**

obs <sup>2,9,25</sup> /cm <sup>-1</sup>	calcd/cm <sup>-1</sup>	sym species	activity	ions involved
350	212	T <sub>2</sub> (1)	IR	Fe+O
	356	T <sub>1</sub>	Raman	Fe+O
				broad structure
319	362	T <sub>2</sub> (2)	IR	Fe+O
440	440	T <sub>2</sub> (3)	IR	Fe+O
500	493	E	Raman	Fe+O
				broad structure
553	523	T <sub>2</sub> (4)	IR	Fe+O
700	695	A <sub>1</sub>	Raman	Fe+O
				broad structure

**TABLE 7: Interatomic Potentials for Hematite**

Short-Range			
interaction	A (eV)	$\rho$ (Å)	C (eV Å <sup>6</sup> )
Fe <sup>3+</sup> ...O <sup>2-</sup>	1102.4	0.329	0
O <sup>2-</sup> ... O <sup>2-</sup>	22764	0.149	40
Shell Model			
	Y (e)	k (eV Å <sup>-2</sup> )	
Fe <sup>3+</sup>	4.97	60.7	
O <sup>2-</sup>	-2.239	200	

**TABLE 8: Calculated and Experimental Crystal Properties for Hematite**

Unit Cell Parameters		
	exp	calcd
a (Å)	5.04	5.09
b (Å)	5.04	5.09
c (Å)	13.77	12.96
$\alpha$ (deg)	90	90
$\beta$ (deg)	90	90
$\gamma$ (deg)	120	120
Atomic Coordinates $\bar{R}3c$		
species	xyz (exp)	xyz (calcd)
Fe <sup>3+</sup>	0	0
	0	0
	0.355	0.359
O <sup>2-</sup>	0.305	0.277
	0	0
	0.25	0.25

Raman spectrum for their sample of maghemite, at  $\sim 350$  cm<sup>-1</sup>,  $\sim 500$  cm<sup>-1</sup>, and  $\sim 700$  cm<sup>-1</sup>. The calculated Raman-active T<sub>1</sub>, E, and A<sub>1</sub> phonons are in good agreement with this observed data. The calculated infrared-active phonons at 442 and 524 cm<sup>-1</sup> are in good agreement with the observed infrared-active phonons reported by Gehring et al.<sup>27</sup> and Bell et al.<sup>2</sup> at 440 and 553 cm<sup>-1</sup>. The lowest energy T<sub>2</sub> modes are calculated at 212 and 362 cm<sup>-1</sup>.

**3.3. The Infrared- and Raman-Active Phonons for Hematite.** The Buckingham potential used for magnetite and maghemite was retained for hematite, but the spring constants used for Fe<sup>3+</sup> and O<sup>2-</sup> have been adjusted compared to the magnetite and maghemite values. The potential shown in Table 7 reproduces the a cell parameter to better than 1% and the c parameter to  $\pm 6\%$  (Table 8).

The observed<sup>28</sup> and calculated Raman-active phonons for hematite are shown in Table 9. Agreement is good for the two A<sub>1g</sub> and four lowest energy E<sub>g</sub> modes but is poor for the highest wavenumber E<sub>g</sub> mode calculated at 467 cm<sup>-1</sup> compared to the observed band at 613 cm<sup>-1</sup>. The Buckingham potential parameters for magnetite do not adequately account for the hematite

**TABLE 9: Calculated and Observed Wavenumbers for Hematite**

obs <sup>26,27</sup> /cm <sup>-1</sup>	calcd/cm <sup>-1</sup>	sym species	activity	ions involved
225	228	A <sub>1g</sub>	Raman	Fe,O
229	290	Eu	IR	Fe,O
247	200	E <sub>g</sub>	Raman	Fe,O
293	294	E <sub>g</sub>	Raman	Fe,O
299	327	E <sub>g</sub>	Raman	Fe,O
310–335	310	Eu	IR	Fe,O
310–335	339	A <sub>2u</sub>	IR	Fe,O
380–400	368	Eu	IR	Fe,O
380–400	378	A <sub>2u</sub>	IR	Fe,O
412	391	E <sub>g</sub>	Raman	Fe,O
440–470	454	Eu	IR	Fe,O
498	447	A <sub>1g</sub>	Raman	Fe,O
613	466	E <sub>g</sub>	Raman	Fe,O

lattice interactions along c, and this results in the anomalously low value for the calculated E<sub>g</sub> phonon.

There is good agreement for the calculated infrared-active phonons when compared to the infrared data of Serna et al.<sup>29</sup>

#### 4. Conclusions

Through use of atomistic simulation, phonon energies and their eigenvectors have been calculated for the infrared- and Raman-active phonons of Fe<sub>3</sub>O<sub>4</sub>,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. Lowering the symmetry in the sequence Fe<sub>3</sub>O<sub>4</sub> >  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> >  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> leads to an increase in the number of calculated and observed Raman-active phonons. This increase in the number of Raman fundamentals can explain the change in the Raman spectrum of Fe<sub>3</sub>O<sub>4</sub> under heating when the following phase transitions have been shown to occur.



Our calculations confirm the Raman results obtained by de Faria et al.,<sup>9</sup> postulating that the Raman spectra of Fe<sub>3</sub>O<sub>4</sub> and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> are each unique. According to our calculations, the observed Raman phonons at similar wavenumber for Fe<sub>3</sub>O<sub>4</sub> and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> have a different atomic origin. For example, each of the given iron oxides has a fundamental in the region 670–700 cm<sup>-1</sup>. The calculated Cartesian displacements show that the A<sub>1g</sub> mode of Fe<sub>3</sub>O<sub>4</sub> (670 cm<sup>-1</sup>) is a mode of oxygen ion displacement only, whereas the A<sub>1</sub> mode of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (700 cm<sup>-1</sup>) is characterized by displacements of both iron and oxygen.

Disagreement between Raman spectra reported for magnetite, maghemite, and hematite may in large part be attributed to the heating effect of the incident laser radiation. Secondary effects will be present due to the nonstoichiometry of iron oxides.

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