Hybrid density functional theory applied to magnetite II: Γ point phonons and vibrational spectra

Charles H. Patterson
School of Physics, Trinity College Dublin, Dublin 2, Ireland

L. V. Gasparov
Department of Chemistry and Physics, University of North Florida, St. John's Bluff Rd. South, Jacksonville, Florida 32224
(Dated: November 18, 2008)

Generalized gradient and B3LYP hybrid density functional theory (DFT) approximations are used to calculate phonons at the Γ point of the Brillouin zone of magnetite (Fe₃O₄). DFT in a generalized gradient approximation (GGA), predicts an itinerant electron ground state for the cubic, Fd3m unit cell observed above the Verwey transition temperature, Tᵥ, and the B3LYP hybrid DFT approximation predicts a charge ordered semiconducting state for the monoclinic P2/c unit cell below Tᵥ. Phonon frequencies predicted for these crystal structures are compared to frequencies from infra-red (IR) conductivity and Raman scattering experiments. The charge ordered state predicted by B3LYP is similar to that found in recent DFT-GGA + Hubbard-U calculations. Charge ordering causes symmetry breaking of force constants on symmetry lowering from the cubic Fd3m unit cell to the P2/c unit cell. This produces frequency splitting of modes which are degenerate in the cubic unit cell and concentration of ion displacements in phonon eigenvectors on particular Fe octahedral B site chains, especially in the highest frequency bands. There is one unstable eigenvector in the B3LYP calculation of the vibrational spectrum of the P2/c unit cell. It is suggested that this instability occurs because the P2/c space group unit cell is an approximation to the actual Cc space group determined by x-ray scattering.

PACS numbers: 63.20.-e, 78.30.-j, 71.15.Mb, 71.30.+h

I. INTRODUCTION

The Verwey transition in magnetite (Fe₃O₄)¹,² is one of the most studied transitions in condensed matter physics. At room temperature, well above the Verwey transition temperature (Tᵥ ~ 120K), Fe₃O₄ has a cubic structure with Fd3m space group symmetry and a lattice constant a₀=8.3939 Å.³ Below Tᵥ it exists in a monoclinic phase which is believed to be charge ordered on the basis of experiment¹–¹³. Several recent density functional theory (DFT) calculations in DFT + self-interaction correction (SIC) or DFT + Hubbard-U schemes have focused on the electronic structure of the low temperature, charge ordered phase¹⁴–²². Density functionals which contain Hartree-Fock (HF) exchange and a density functional approximation to exchange, with weights which sum to unity, are known as hybrid functionals. In the preceding paper (which is referred to below as I²³), results of DFT and B3LYP²⁴,²⁵ hybrid DFT calculations of the electronic and crystal structures of Fe₃O₄ were presented. An analysis of charge order in Fe₃O₄ predicted by the B3LYP functional was also given. There is generally good agreement between DFT + Hubbard U and hybrid DFT methods in the patterns of both charge and orbital order in the monoclinic phase (see I for a comparison).

DFT calculations presented in I in the generalized gradient approximation without a Hubbard-U term in the Hamiltonian predict the high temperature Fd3m phase to be an itinerant electron metal. The monoclinic phase has Cc space group symmetry and a √2a₀ x √2a₀ x 2a₀ unit cell, four times larger than the cubic, high temperature cell. Neutron and x-ray diffraction studies³–²⁶ have refined the low temperature, monoclinic cell using a smaller a₀/√2 x a₀/√2 x 2a₀, monoclinic cell with Pmca²⁶, Pmc2₁,²⁶ or P2/c symmetry³. Equilibrium structures with P2/c symmetry have been calculated using DFT + Hubbard U¹⁵,¹⁶,¹₉ and hybrid DFT methods²³. There is remarkably good agreement between bond length distortions in the x-ray structure refinement of the monoclinic phase with assumed P2/c symmetry⁴ and those predicted by the hybrid DFT calculation in I (c.f. equal octahedral site Fe-O bond lengths in the high symmetry cubic phase). Group theoretical arguments have been applied to the transition between the Fd3m and P2/c structures to show that at least two order parameters must be involved in a transition¹⁹,²⁰ from Fd3m to P2/c crystal symmetries.

Early measurements of the Infra-red (IR) vibrational spectrum of Fe₃O₄ were reported by Waldron in 1955²⁷. White and De Angelis²⁸ and Verble²⁹ assigned the Raman spectrum of Fe₃O₄ and many subsequent studies of both the IR³⁰–³² and Raman spectra³³–³⁴ have been reported. Several calculations of the phonon modes of the Fd3m cubic structure based on DFT have been reported recently¹⁹,²⁰,³⁵. Here we report calculations of Γ point phonon modes of both the cubic and monoclinic structures of Fe₃O₄ using either Perdew-Wang DFT-GGA³⁶ or hybrid DFT functionals. The IR conductivity is calculated using a Lorentz oscillator model and compared to recent experimental data.³¹ Densities
of phonon modes of appropriate symmetry are compared to Raman spectra\(^{34}\). Phonon calculations for both structures were performed using the Crystal electronic structure package\(^{37}\) and employed the same basis set and similar computational conditions. It is therefore possible to make a direct comparison between the phonon modes predicted by the two calculations.

![Diagram of Crystal Structure](image)

**FIG. 1:** (Color online) Crystal structure of magnetite in the monoclinic \(P2/c\) unit cell with labelling scheme used in the text.

The unit cell of the monoclinic \(Cc\) phase of \(\text{Fe}_3\text{O}_4\) below \(T_V\) contains 224 ions and contains too many ions for a phonon calculation using the Crystal package on currently available computers. The unit cell of the \(P2/c\) phase contains 56 ions; the phonon calculation for the smaller cell presented here is used to identify the character of the phonon modes which are observed in the low temperature phase of \(\text{Fe}_3\text{O}_4\). A phonon calculation can also be used as a test of the stability of any equilibrium crystal structure since a saddle point on the potential energy surface manifests itself as an imaginary frequency of one or more phonon modes. Bond length distortions, which occur on going from the \(Fd\bar{3}m\) to the \(P2/c\) phase, break site symmetries of \(\text{Fe}\) and \(\text{O}\) ions. Phonon mode frequencies, which are degenerate in the \(Fd\bar{3}m\) phase, split in the \(P2/c\) phase and eigenvector amplitudes become concentrated on specific sites.

In the \(Fd\bar{3}m\) \(\text{Fe}_3\text{O}_4\) unit cell there are six \(\text{Fe}\) ions in two equivalent tetrahedral \(A\) sites and four equivalent octahedral \(B\) sites. All eight \(\text{O}\) ions are in equivalent sites. The primitive unit cell for the \(P2/c\) phase (Fig. 1) contains eight \(\text{Fe}^{3+}\) ions with tetrahedral oxygen coordination in two crystallographic sites denoted \(A1\) and \(A2\), and 24 \(\text{Fe}^{2+}\) and \(\text{Fe}^{3+}\) ions with octahedral coordination in six crystallographic sites denoted \(B1\), \(B1b\), \(B2\), \(B2b\), \(B3\), \(B4\). The same notation is used here as was used by Wright et al. in Ref. [3]. The arrangement of \(\text{Fe}\) ions in \(B\) sites consists of chains of \(B1\) and \(B2\) ions parallel to the \(a\) lattice translation vector, connected by \(\text{O}\) ions with 90° \(\text{Fe}-\text{O}-\text{Fe}\) bond angles. There are similar mixed chains of \(B3\) and \(B4\) ions parallel to the \(b\) vector. \(B1\) and \(B1b\) and \(B2a\) and \(B2b\) ion pairs are almost crystallographically equivalent\(^{32,33}\). It is convenient to think of the \(P2/c\) unit cell of \(\text{Fe}_3\text{O}_4\) in terms of chains of corner sharing \(\text{Fe}_2\text{O}_2\) units, stacked in layers in the order \(B1, B3+B4, B2, B3+B4\), connected by \(\text{Fe}\) \(A\) site ions and alternating in direction from layer to layer (Fig. 1). There are eight \(\text{O}\) sites in the \(P2/c\) cell of \(\text{Fe}_3\text{O}_4\), labelled \(O1\)-\(O4\) and \(O5a\), \(O5b\), \(O6a\) and \(O6b\). Ions labelled \(a\) and \(b\) are in nearly equivalent sites. Where both \(a\) and \(b\) sites are referred to together in what follows, the \(a,b\) designation of sites is omitted.

The original Verwey model\(^{38}\) of charge order is one in which Coulomb repulsions of ordered \(\text{Fe}^{2+}\) and \(\text{Fe}^{3+}\) on octahedral \(B\) sites are minimized. The problem of minimization of Coulomb repulsions in magnetite was reduced to a simple criterion by Anderson\(^{39}\), that each \(\text{Fe}\) tetrahedron in the unit cell (formed e.g. from two \(B1\) ions in one chain and \(B3\) and \(B4\) ions in the chain beneath) should contain two \(\text{Fe}^{2+}\) and two \(\text{Fe}^{3+}\) ions only. The pattern of charge order which has been found in first principles calculations\(^{14-16,23}\) is one where \(B1\) and \(B4\) sites are formally \(\text{Fe}^{2+}\) and \(B2\) and \(B3\) sites are formally \(\text{Fe}^{3+}\). This pattern does not meet Anderson’s criterion, but charge order is predicted in calculations and, as noted above, evidence for it is found in experiment.

**II. RESULTS**

A. Lorentz oscillator model for IR conductivity

In order to compare results of phonon calculations to phonons observed as peaks in IR conductivity measurements\(^{31}\), the IR conductivity was calculated using a Lorentz oscillator (LO) model. The conductivity tensor \(\sigma(\omega)\) is given by a sum over phonon modes,

\[
\sigma(\omega/\text{cm}^{-1}) = \frac{\omega}{60e^2V} \sum_i \frac{Z_i Z_i^T}{(\omega_i^2 - \omega^2)^2 + (\gamma_i \omega)^2} \tag{1}
\]

where \(\omega_i\) are phonon frequencies, \(\gamma\) is a damping parameter, chosen to be 6 cm\(^{-1}\), \(z_i\) are Born charges, \(x_{ij}\) is the \(i^{th}\) component of the \(j^{th}\) phonon eigenvector, \(m_j\) are atomic masses and \(V\) is the unit cell volume. Born charges of +2.67e and -2.00e were used for all \(\text{Fe}\) and \(\text{O}\) ions, respectively.
Minimum energy crystal structures were calculated for Fe₃O₄ in the Fd̅3m and P2/c spacegroup unit cells. Full details of these structures are given in I. DFT-GGA or hybrid DFT functionals were used in both cases. DFT-GGA predicts the Fd̅3m structure to be an itinerant electron metal with a lattice constant \( a = 8.3770 \) Å and B3LYP predicts the P2/c structure to be a charge ordered semiconductor, with lattice constants of \( a = 6.0078 \), \( b = 6.0143 \), \( c = 16.9235 \) Å and \( \gamma = 90.0000^\circ \). B3LYP predicts charge localization and structure symmetry breaking in the Fd̅3m structure when the total lattice + electronic energy is minimized and symmetry constraints on atomic positions are not enforced. Experimental lattice constants for the P2/c structure are \( a = 5.9444 \), \( b = 5.9247 \), \( c = 16.7750 \) Å, \( \gamma = 90.236^\circ \). Phonon calculations on the P2/c phase reported here were performed using the energy minimized structure with lattice constants fixed at the experimental values. A brief discussion on the dependence of phonon frequencies on lattice parameters is given in the Appendix.

### C. Phonons in the high temperature Fd̅3m unit cell

Symmetry analysis of the Fd̅3m structure of magnetite shows that the 42 vibrational + translational modes consist of 12 Raman active modes \((A_g + E_g + 3 T_{2g})\), 15 IR active modes \( (5 T_{2u})\), 3 of which are translational modes and 15 optically inactive modes \( (2 B_u + 2 E_u + T_{1u} + 2 T_{2u})\). Mode frequencies from experiment, the present work and other DFT-GGA calculations are shown in Table I. Basis sets, \( k \) point sampling conditions, etc. used in calculations reported in this work are described in the Appendix.

TABLE I: Phonon frequencies in Fd̅3m magnetite from experiment and DFT-GGA calculations in cm\(^{-1}\).

<table>
<thead>
<tr>
<th>DFT(^a)</th>
<th>DFT(^b)</th>
<th>DFT(^c)</th>
<th>Expt.(^d)</th>
<th>Irrep. Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>147</td>
<td>136</td>
<td>148</td>
<td>200</td>
<td>T(_{2u})</td>
</tr>
<tr>
<td>196</td>
<td>161</td>
<td>188</td>
<td>193</td>
<td>T(_{2g})</td>
</tr>
<tr>
<td>204</td>
<td>170</td>
<td></td>
<td></td>
<td>E(_u)</td>
</tr>
<tr>
<td>208</td>
<td>195</td>
<td>235</td>
<td>308</td>
<td>E(_u)</td>
</tr>
<tr>
<td>334</td>
<td>267</td>
<td></td>
<td>350</td>
<td>T(_{1u})</td>
</tr>
<tr>
<td>343</td>
<td>309</td>
<td></td>
<td></td>
<td>T(_{1u})</td>
</tr>
<tr>
<td>353</td>
<td>287</td>
<td>293</td>
<td></td>
<td>A(_{2u})</td>
</tr>
<tr>
<td>363</td>
<td>265</td>
<td>308</td>
<td></td>
<td>A(_{2u})</td>
</tr>
<tr>
<td>389</td>
<td>323</td>
<td>327</td>
<td>350</td>
<td>T(_{1u})</td>
</tr>
<tr>
<td>410</td>
<td>344</td>
<td></td>
<td></td>
<td>T(_{2u})</td>
</tr>
<tr>
<td>465</td>
<td>400</td>
<td>450</td>
<td></td>
<td>T(_{2g})</td>
</tr>
<tr>
<td>522</td>
<td>423</td>
<td></td>
<td></td>
<td>E(_u)</td>
</tr>
<tr>
<td>565</td>
<td>525</td>
<td>540</td>
<td></td>
<td>T(_{2g})</td>
</tr>
<tr>
<td>584</td>
<td>589</td>
<td>670</td>
<td></td>
<td>A(_{1g})</td>
</tr>
<tr>
<td>657</td>
<td>598</td>
<td></td>
<td></td>
<td>A(_{2u})</td>
</tr>
</tbody>
</table>

\(^a\)This work
\(^b\)Piekarz et al. Ref. [19]
\(^c\)Handke et al. Ref. [35]
\(^d\)Gasparov et al. Ref.[31]

IR active modes are found in experiment at room temperature at 200, 350 and 560 cm\(^{-1}\); the mode around 200 cm\(^{-1}\) is weak in the most recent data\(^3\) and is completely absent from the earlier data of Degiorgi et al.\(^30\). The modes at 350 and 560 cm\(^{-1}\) are the main features in the vibrational IR conductivity spectrum at room temperature. The three DFT-GGA calculations in Table I predict the lowest T\(_{1u}\) mode frequency at between 161 and 196 cm\(^{-1}\). Higher T\(_{1u}\) modes are predicted to lie between 309 and 343 cm\(^{-1}\), between 323 and 389 cm\(^{-1}\) and between 538 and 562 cm\(^{-1}\). The two highest frequency T\(_{1u}\) modes carry the great majority of the IR oscillator strength in an LO model of the IR conductivity. Frequencies for these two modes are predicted to be 389 and 562 cm\(^{-1}\) in this work; these compare well with experimental values of 350 and 560 cm\(^{-1}\).\(^31\) The IR spectrum at room temperature therefore consists of: a T\(_{1u}\) mode at 200 cm\(^{-1}\) with little oscillator strength; a second T\(_{1u}\) mode, predicted to lie at 343 cm\(^{-1}\), is a weak shoulder in the strongest mode, which is observed at 350 cm\(^{-1}\) and predicted at 389 cm\(^{-1}\); the highest T\(_{1u}\) mode is at 560 cm\(^{-1}\), in good agreement with the predicted value of 562 cm\(^{-1}\). Ion displacements in IR active phonons in Fd̅3m Fe₃O₄ are illustrated in Fig. 2.

![Color online] IR active phonon mode eigenvectors of T\(_{1u}\) symmetry from DFT-GGA calculation on Fe₃O₄ in the Fd̅3m unit cell. Mode frequencies are: (a) 196 cm\(^{-1}\), (b) 343 cm\(^{-1}\), (c) 389 cm\(^{-1}\), and (d) 562 cm\(^{-1}\). Displacements of O ions about tetrahedrally coordinated Fe\(^{3+}\) A site ions are shown separately for each mode.

Raman active modes are observed in experiment at room temperature at 193, 308, 540 and 670 cm\(^{-1}\) by...
Gasparov et al.\textsuperscript{31} and at 193, 306, 538 and 668 cm\textsuperscript{-1} by Shebanova and Lazor\textsuperscript{34}. There is therefore good agreement between these recent studies. Shebanova and Lazor have assigned the modes at 193 and 538 cm\textsuperscript{-1} to $T_{2g}$ modes and the modes at 306 and 668 cm\textsuperscript{-1} to $E_g$ and $A_g$ modes, respectively. They assigned a weak feature observed at 490 cm\textsuperscript{-1} in another study\textsuperscript{10} to the third $T_{2g}$ mode. There is a weak peak at 450 cm\textsuperscript{-1} in the room temperature data in Ref. [31]. The ranges of positions of Raman active modes predicted by the DFT calculations in Table I are 195 to 235, 400 to 465 and 525 to 565 cm\textsuperscript{-1} for $T_{2g}$ modes, 265 to 363 cm\textsuperscript{-1} for the $E_g$ mode and 584 to 589 cm\textsuperscript{-1} for the $A_g$ mode. The assignment by Shebanova and Lazor\textsuperscript{34} is therefore in agreement with the mode frequencies from these DFT calculations.

**FIG. 3:** (Color online) Raman active phonon mode eigenvectors from DFT-GGA calculations on Fe$_3$O$_4$ with in the $Fd\bar{3}m$ unit cell. Mode frequencies and symmetries are: (a) 223 cm\textsuperscript{-1} $T_{2g}$, (b) 465 cm\textsuperscript{-1} $T_{2g}$, (c) 565 cm\textsuperscript{-1} $T_{2g}$, (d) 363 cm\textsuperscript{-1} $E_g$ and (e) 584 cm\textsuperscript{-1} $A_g$. Displacements of O ions about tetrahedrally coordinated Fe\textsuperscript{3+} A site ions are shown separately for each mode.

**D. Phonons in the low temperature $P2/c$ unit cell**

There are 56 ions in the $P2/c$ unit cell of Fe$_3$O$_4$; the 168 vibrational + translational modes at the $\Gamma$ point of the Brillouin zone consist of 38 $A_g + 40 B_g + 44 A_u + 46 B_u$ modes. Symmetry operations for the $P2/c$ space group with a unique $b$ axis are $E, C_2(y)+0.5z, i$ and $\sigma_b+0.5z$. $A(B)$ modes are even(odd) with respect to the $C_2$ rotation, $g(u)$ modes are even(odd) with respect to inversion and the $A_u$ and $B_u$ modes are even with respect to the mirror plane and the $A_u$ and $B_u$ modes are odd. Fig. 1 shows that B1a Fe ions lie on the $C_2$ axis and B2 Fe ions almost lie in the mirror plane. $A_u$ and $B_u$ modes are IR active and couple to electric fields polarized along the $y$ and $x,z$ axes, respectively, when the unique axis is $b$ and $x$, $y$ and $z$ axes are parallel or almost parallel to the $a$, $b$ and $c$ axes. $A_g$ and $B_g$ modes are Raman active. $A_g$ modes are detected in an $XX$ experimental geometry\textsuperscript{34} in which incident and scattered radiation have the same polarization, while $B_g$ modes are detected in an $XY$ geometry where polarizations of incident and scattered radiation are at right angles.

Experimental IR conductivity data for Fe$_3$O$_4$ at 40K from Ref. [31] are reproduced in Fig. 4 and show two strong bands between 300 and 400 cm\textsuperscript{-1} and between 550 and 650 cm\textsuperscript{-1}. There are also bands around 100 and 250 cm\textsuperscript{-1}. The LO model in Eq. 1 was used to calculate the conductivity of Fe$_3$O$_4$ using $A_u$ and $B_u$ phonon eigen-modes. Vibrational frequencies (and other properties such as band gap\textsuperscript{41}) predicted by hybrid DFT methods depend quite sensitively on the weight of HF exchange used in calculations; in the case of Fe$_3$O$_4$, increasing the weight from 20% (B3LYP) to 30% increases mode frequencies in Fe$_3$O$_4$ by 10%. When the experimental data and the results of the LO model are compared, it is clear that peaks in the IR conductivity from the LO model are too high in frequency by about 5%. The results of the LO model and the experimental data are plotted in Fig. 4 with scales that differ by 5% so that the scaled LO model curve can be directly compared to experiment. The main LO model curve in Fig. 4 shows orientationally averaged conductivities for electric fields applied along three Cartesian directions. The inset to Fig. 4 shows LO model conductivities for each applied field direction. Inspection of the inset shows that the modes in the higher frequency IR band occur as split pairs for fields along the $x$ and $y$ ($a$ and $b$ crystallographic) directions. This splitting arises because of charge order on octahedral B sites.

The IR active $T_{1u}$ mode predicted by DFT-GGA at 389 cm\textsuperscript{-1} in the $Fd\bar{3}m$ unit cell and observed in experiment around 350 cm\textsuperscript{-1} (Table I), is replaced by 10 $A_u$ and 12 $B_u$ modes in the range 300 - 400 cm\textsuperscript{-1} in the B3LYP calculation in Fig. 6a and b. The mode predicted by DFT-GGA at 562 cm\textsuperscript{-1} in the $Fd\bar{3}m$ unit cell and observed in experiment around 560 cm\textsuperscript{-1} (Table II), is replaced by 5 $A_u$ and 5 $B_u$ modes in the range 550 - 650 cm\textsuperscript{-1} in the B3LYP calculation. Mode frequencies
TABLE II: Strongly IR active phonon modes in \( P2/c \) magentite from B3LYP calculations. Ion sites on which phonon eigenvectors amplitudes are primarily concentrated and mode frequencies in \( \text{cm}^{-1} \) are given.

<table>
<thead>
<tr>
<th>Freq.</th>
<th>Irrep.</th>
<th>Eigenvector</th>
</tr>
</thead>
<tbody>
<tr>
<td>570</td>
<td>( A_u )</td>
<td>B4 O4 O5 O6</td>
</tr>
<tr>
<td>389</td>
<td>( A_u )</td>
<td>B2 B3 O1 O3 O5 O6</td>
</tr>
<tr>
<td>349</td>
<td>( B_u )</td>
<td>B2 O4</td>
</tr>
<tr>
<td>373</td>
<td>( B_u )</td>
<td>B2 B3 O1 O4 O5 O6</td>
</tr>
<tr>
<td>559</td>
<td>( A_u )</td>
<td>O3 O4</td>
</tr>
<tr>
<td>617</td>
<td>( A_u )</td>
<td>O1 O2</td>
</tr>
<tr>
<td>573</td>
<td>( B_u )</td>
<td>O5</td>
</tr>
<tr>
<td>627</td>
<td>( B_u )</td>
<td>B2 O6</td>
</tr>
</tbody>
</table>

![Graph of IR conductivity of Fe\textsubscript{3}O\textsubscript{4} at 40K reproduced from Ref. 31 (dotted curve) and from an LO model using phonon modes from B3LYP calculation on Fe\textsubscript{3}O\textsubscript{4} in the P2/c unit cell (solid curve). The orientationally averaged spectrum from the LO model is drawn with a scale which differs from that for experiment by 5%, as explained in the text. Inset shows the decomposition of the averaged IR conductivity into components excited by electric field vectors aligned with Cartesian x, y and z axes.](image)

Inspection of the \( A_u \) mode eigenvectors in Fig. 5a,b shows that ion displacements in these modes are concentrated on specific B site chains. The mode at 370 \( \text{cm}^{-1} \) is concentrated on B4, O5 and O6 sites of the B3/B4 chain and especially on O4 sites in the B2 chain (Table II). The mode at 389 \( \text{cm}^{-1} \) is concentrated on B3, O5 and O6 sites in the B3/B4 chain and also the B2 and O3 sites of the B2 chain. These modes are similar in character bu but are concentrated either on O3 or O4 ions in the B2 chain. The 349 \( \text{cm}^{-1} B_u \) mode eigenvector in Fig. 5c is strongly concentrated on B2 and O4 sites in the B2 chains and the 374 \( \text{cm}^{-1} \) mode eigenvector is spread over all B site layers. Charge order must induce changes in force constants for interactions between Fe ions and their O neighbors. Symmetry breaking in magnitudes of force constants on going from the cubic \( Fd3m \) unit cell to the \( P2/c \) monoclinic cell will result in ion displacements in specific modes becoming concentrated on specific ions and splitting of frequencies of phonons which are degenerate in the cubic unit cell. The extent of concentration of modes on specific O ions is much greater for the higher frequency IR and Raman active bands which predominantly involve O ion displacements.

The IR conductivity band between 550 and 650 \( \text{cm}^{-1} \) is generated by modes which are essentially completely concentrated on O ions. They consist of out-of-phase A site Fe-O stretching in both the \( Fd3m \) and \( P2/c \) unit cells. In the \( P2/c \) unit cell, modes are concentrated on O ions in particular B site chains, whereas in the \( Fd3m \) unit cell, symmetry dictates that displacement amplitudes on each O ion are equal in magnitude. The 559 \( \text{cm}^{-1} A_u \) mode in Fig. 6a is concentrated on O3 and O4 ions in B2 chains, the 617 \( \text{cm}^{-1} A_u \) mode is concentrated on O1 and O2 ions in B1 chains, the 573 \( \text{cm}^{-1} B_u \) mode is concentrated on O5 ions and the 627 \( \text{cm}^{-1} B_u \) mode is concentrated on B2 and O6 ions.

The pattern of concentration of ion displacements on specific sites can be explained by charge order on B sites. The charge order found in I shows that Fe ions in B2 chains are formally Fe\textsuperscript{3+} while Fe ions in B1 chains are formally Fe\textsuperscript{2+}. The \( A_u \) modes in Fig. 5a and b involve stretching of B2 site Fe-O3 and Fe-O4 bonds and B1 site Fe-O1 and Fe-O2 bonds. In this case, each chain is homogeneously charge ordered and force constants differ sufficiently between chains so that ion displacements in the two modes localize on either chain. The \( B_u \) modes in Fig. 6c and d are concentrated on B3/B4 chains but are split between O5 and O6 sites. O5 ions are bonded to B2 sites (Fe\textsuperscript{3+}) in the chain above or below, while O6 ions are bonded to B1 sites (Fe\textsuperscript{2+}) above or below. This difference in environment is sufficient to split the mode frequencies by 54 \( \text{cm}^{-1} \). Obviously, the greater the extent of charge ordering, the larger the splitting will be.

Since single modes in the \( Fd3m \) phase are replaced by multiple modes in the \( P2/c \) phase, broadening of IR band linewidths in experiment might be expected on cooling through \( T_V \). Linewidths and frequency shifts in IR and Raman active modes which accompany the Verwey tran-
sition were reported previously. The 300 - 400 cm\(^{-1}\) band linewidth increases from 24 to 39 cm\(^{-1}\) and the 550 - 650 cm\(^{-1}\) band linewidth increases from 26 to 36 cm\(^{-1}\) on cooling through \(T_V\). The experimental linewidth is too broad to distinguish individual modes in the \(P2/c\) phase, but the 300 - 400 cm\(^{-1}\) band is certainly more asymmetric below \(T_V\). However, the linewidth of the strong Raman line around 670 cm\(^{-1}\) actually decreases from 30 to 20 cm\(^{-1}\) on cooling through \(T_V\).

The Raman spectrum for Fe\(_3\)O\(_4\) at 5 K is shown in Fig. 7 for both XX and XY experimental geometries. Changes in the Raman spectrum in the XX experimental geometry on warming to 300K are shown in the inset to Fig. 7. There are dramatic changes in the Raman spectrum in the XX experimental geometry on cooling below \(T_V\), in particular a mode appears around 165 cm\(^{-1}\), a broad band of modes appears between 200 and 500 cm\(^{-1}\) and a shoulder to the \(A_g\) mode at 670 cm\(^{-1}\) appears around 650 cm\(^{-1}\). It is not possible to calculate Raman cross sections using the Crystal package. Instead the \(A_g\) and \(B_g\) densities of modes at the \(\Gamma\) point are compared to experimental spectra by representing each mode as a Lorentz oscillator with a FWHM of 6 cm\(^{-1}\). Frequency axis scales which differ by 5% for B3LYP calculation and experimental mode frequencies are used in the same manner as for the IR spectrum in Fig. 4. There are less dramatic changes in the XY geometry experimental spectrum (Fig. 7) on cooling through \(T_V\). There is reasonable agreement
between the density of modes from the B3LYP calculation and the positions of experimental lines in the XX and XY geometries, except below 250 cm\(^{-1}\) in the XY geometry.

![Graph showing Raman spectrum vs temperature](attachment:image.png)

FIG. 7: Raman spectrum of Fe\(_3\)O\(_4\) at 5K and \(A_g\) and \(B_g\) mode densities from B3LYP calculation on Fe\(_3\)O\(_4\) in the \(P2_1/c\) unit cell. Experimental spectra measured in XX and XY geometries are reproduced from Ref. 31. Mode frequencies from the DFT-GGA calculation in this work to lie at 565 and 584 cm\(^{-1}\) as explained in the text. Inset shows the variation of the Raman spectrum with temperature below and above \(T_V\).

The most intense Raman lines in the room temperature spectrum of Fe\(_3\)O\(_4\) are the \(T_{2g}\) and \(A_g\) modes predicted by the DFT-GGA calculation in this work to lie at 565 and 584 cm\(^{-1}\), respectively. Experimental lines are observed at 540 and 670 cm\(^{-1}\). The B3LYP calculation on Fe\(_3\)O\(_4\) in the \(P2_1/c\) unit cell predicts 4 \(A_g\) and 4 \(B_g\) modes between 560 and 640 cm\(^{-1}\) and 4 \(A_g\) and 4 \(B_g\) modes between 650 and 800 cm\(^{-1}\). These groups of modes replace the highest frequency \(T_{2g}\) and \(A_g\) modes observed above \(T_V\).

Raman active modes between 560 and 640 cm\(^{-1}\) differ in character from the 565 cm\(^{-1}\) \(T_{2g}\) modes in \(Fd3m\) Fe\(_3\)O\(_4\) (Fig. 3). The 8 \(A_g\) and \(B_g\) modes between 560 and 640 cm\(^{-1}\) consist of out-of-phase breathing motions along A site Fe-O bonds, similar to the \(A_u\) and \(B_u\) IR active modes shown in Fig. 6, but are even rather than odd with respect to inversion. The four \(B_g\) modes at 560 and 640 cm\(^{-1}\) are shown in Fig. 8. The pattern of concentration of eigenvector amplitude for the \(B_g\) modes at 574 and 631 is the same as for the \(A_g\) and \(B_g\) IR active modes between 559 and 627 cm\(^{-1}\) (Table II). Ion displacements are concentrated on O3 + O4 ions in B2 chains, O5 ions in B3/B4 chains, O1 + O2 ions in B1 chains and O6 ions in B3/B4 chains.

![Graph showing Raman active phonon eigenvectors](attachment:image2.png)

FIG. 8: (Color online) \(B_g\) Raman active phonon eigenvectors from B3LYP calculation on Fe\(_3\)O\(_4\) in the \(P2_1/c\) unit cell between 560 and 640 cm\(^{-1}\). (a) 574 cm\(^{-1}\), (b) 578 cm\(^{-1}\), (c) 615 cm\(^{-1}\) and (d) 631 cm\(^{-1}\).

The \(A_g\) mode at 584 cm\(^{-1}\) in the DFT-GGA calculation on Fe\(_3\)O\(_4\) in the \(Fd3m\) unit cell consists of breathing motions of A site Fe-O bonds. The in-phase breathing motion induces large electronic polarizability changes with changes in phonon coordinate and hence this is the mode with the greatest Raman cross section. The 8 \(A_g\) and \(B_g\) modes between 650 and 800 cm\(^{-1}\) also consist of breathing motions of A site Fe-O bonds. Mode frequencies and concentration of ion displacements on specific O ions are given in Table III. Eigenvectors corresponding to the \(B_g\) mode at 693 cm\(^{-1}\) and the \(A_g\) mode at 720 cm\(^{-1}\) are shown in Fig. 9. They have a breathing character about A site Fe\(^{3+}\) sites but concentration of the modes on particular O sites results in a 'half-breathing' mode.
TABLE III: Raman active $A_g$ and $B_g$ phonon modes between 560 and 640 cm$^{-1}$ and between 650 and 800 cm$^{-1}$ from B3LYP calculation on Fe$_3$O$_4$ in the $P2/c$ unit cell. Ion sites on which phonon amplitudes are primarily concentrated and mode frequencies in cm$^{-1}$ are given.

<table>
<thead>
<tr>
<th>Freq.</th>
<th>Irrep.</th>
<th>Eigenvector</th>
</tr>
</thead>
<tbody>
<tr>
<td>581</td>
<td>$A_g$</td>
<td>O2 O3 O6</td>
</tr>
<tr>
<td>595</td>
<td>$A_g$</td>
<td>O1 O2</td>
</tr>
<tr>
<td>624</td>
<td>$A_g$</td>
<td>O7 O6</td>
</tr>
<tr>
<td>626</td>
<td>$A_g$</td>
<td>O2 O3 O4</td>
</tr>
<tr>
<td>574</td>
<td>$B_g$</td>
<td>O3 O4</td>
</tr>
<tr>
<td>578</td>
<td>$B_g$</td>
<td>O5</td>
</tr>
<tr>
<td>615</td>
<td>$B_g$</td>
<td>O1 O2</td>
</tr>
<tr>
<td>631</td>
<td>$B_g$</td>
<td>O6</td>
</tr>
<tr>
<td>650</td>
<td>$A_g$</td>
<td>O2 O5b</td>
</tr>
<tr>
<td>720</td>
<td>$A_g$</td>
<td>O5 O6</td>
</tr>
<tr>
<td>733</td>
<td>$A_g$</td>
<td>O3 O4</td>
</tr>
<tr>
<td>775</td>
<td>$A_g$</td>
<td>O1 O2 O6</td>
</tr>
<tr>
<td>639</td>
<td>$B_g$</td>
<td>O2 O5</td>
</tr>
<tr>
<td>693</td>
<td>$B_g$</td>
<td>O3 O4</td>
</tr>
<tr>
<td>731</td>
<td>$B_g$</td>
<td>O2 O5</td>
</tr>
<tr>
<td>759</td>
<td>$B_g$</td>
<td>O1 O2 O6</td>
</tr>
</tbody>
</table>

FIG. 9: (Color online) Raman active phonon eigenvectors from B3LYP calculation on Fe$_3$O$_4$ in the $P2/c$ unit cell between 650 and 800 cm$^{-1}$. (a) 720 cm$^{-1}$ ($A_g$), (b) 693 cm$^{-1}$ ($B_g$).

III. DISCUSSION AND SUMMARY

The nature of the Verwey transition has been debated over many years$^{1,3,4,8,14,17,20,39,42}$. While there is an abrupt change in electric conductivity at $T_\mathrm{V}$, by about two orders of magnitude$^1$, other probes such as neutron diffuse scattering indicate that there are strong fluctuations in the cubic phase well above $T_\mathrm{V}$. Neutron diffuse scattering extends up to 100 K above $T_\mathrm{V}$ and disappears abruptly below $T_\mathrm{V}$.$^{12,13}$ It has been proposed$^{42}$ that the electronic and crystal structure symmetry breaking about Fe B sites, which is observed in Fe$_3$O$_4$ below $T_\mathrm{V}$, is actually present above $T_\mathrm{V}$. Models including existence of ‘molecular polarons’$^{13}$ and dynamical distortions$^{42}$ which condense at $T_\mathrm{V}$ have been advanced. In this scenario the Verwey transition is essentially an ordering of the lattice polarons which form about Fe B sites with an extra electron, once the thermal energy of the polarons is low enough to allow them to condense. This ordering would then be accompanied by the two orders of magnitude drop in conductivity which occurs on cooling through $T_\mathrm{V}$. In the work reported here, it has been shown that the highest frequency breathing mode phonons in Fe$_3$O$_4$ below $T_\mathrm{V}$ are localized in layers. This localization may have an important part to play in the drop in conductivity at $T_\mathrm{V}$.

If the evolution of IR and Raman spectra through $T_\mathrm{V}$ is examined in the context of this model, the following observations can be made: linewidths of the two main IR active modes above $T_\mathrm{V}$ at 350 and 600 cm$^{-1}$ are fairly broad at 24 and 26 cm$^{-1}$, respectively$^{41}$. These widths are large, but are not much greater than linewidths in other spinels without charge order$^{43}$. Increases in linewidth on cooling through $T_\mathrm{V}$ in this scenario must be due to charge ordering, which produces the splitting of frequencies found in the calculations reported above; the Raman spectrum at 125 K$^{35}$ is essentially the same as the spectrum at 300 K in terms of the number of modes, but the linewidth of the $E_g$ mode around 300 cm$^{-1}$ is very broad ($\sim$100 cm$^{-1}$) just above $T_\mathrm{V}$ at 125 K, suggesting a degree of disorder about Fe B sites, and evolves into the broad band of modes between 200 and 500 cm$^{-1}$ on cooling below $T_\mathrm{V}$. Extra peaks in the spectrum appear abruptly between 120 and 116 K and are fully established at 100 K.

The most striking finding in the work reported here is that phonons in the highest IR band and two highest Raman bands are concentrated on specific B site chains in the low temperature phase and that there are splittings in mode frequencies by $\sim$ 50 cm$^{-1}$ for the 565 cm$^{-1}$ mode (540 cm$^{-1}$ in experiment) and by $\sim$ 120 cm$^{-1}$ for the 584 cm$^{-1}$ mode (670 cm$^{-1}$ in experiment). The Raman spectrum below $T_\mathrm{V}$ shows a line narrowing by 10 cm$^{-1}$ and new modes appear either as distinct peaks or shoulders to strong peaks. These additional peaks may be the frequency split peaks predicted in these calculations. Presumably one mode retains most of the Raman scattering cross section, but other frequency-split modes also have some cross section. Such a redistribution of scattering cross section may explain the observed narrowing of the band observed at 670 cm$^{-1}$ by 10 cm$^{-1}$ when Fe$_3$O$_4$ is cooled through $T_\mathrm{V}$. Charge ordering in Fe$_3$O$_4$ has been shown to have a predominant [001] charge density modulation accompanied by a weaker [00$\frac{1}{2}$] modulation$^2$; magnetic inelastic neutron scattering from Fe$_3$O$_4$ exhibits a
7 meV gap in the spin wave spectrum midway to the Brillouin zone boundary, for \( \mathbf{q} \) vectors parallel to the \( c \) axis. It is therefore not surprising to find strong modulations of ion displacements in phonon modes along the \( c \) axis. Further experimental and theoretical work, including computed Raman cross sections, is needed to resolve the number and polarization of additional modes which are observed below \( T_V \) around 600 cm\(^{-1}\).

The charge order predicted by \( \text{B3LYP in } \text{Fe}_3\text{O}_4 \) and described in detail in I is essentially the same as that predicted by a number of recent DFT + Hubbard U studies\(^{14,15,21}\). In I it was shown that the extent of charge order predicted by \( \text{B3LYP is overestimated} \) compared to experimentally determined values, but that it is not grossly overestimated. The reason for this is that the weight of HF exchange used in the \( \text{B3LYP functional} \) is too large; inclusion of HF exchange causes electrons to localize on Fe B sites (even in the cubic \( Fd\bar{3}m \) unit cell) and creates a band gap when the lattice relaxes. Furthermore, increasing the weight of HF exchange in the functional causes predicted vibrational frequencies to increase. The \( \text{B3LYP hybrid functional} \) has a weighting factor of 0.2 for HF exchange, but for narrow gap oxides such as \( \text{Fe}_3\text{O}_4 \) a smaller weight is required, probably 0.15. Thus the overestimate in vibrational frequencies may be attributed to too large a weight for HF exchange (see Appendix).

There is one unstable mode of \( \text{A}_g \) symmetry in the phonon calculation on \( \text{Fe}_3\text{O}_4 \) in the \( P2/c \) unit cell. It is concentrated mainly on Fe A2 and B3 and O6 sites and displacements are mainly parallel to the \( b \) axis. The Crystal package computes analytic derivatives of the total energy with respect to ion displacement\(^{45,46} \) (i.e. forces on the ion, including Pulay forces\(^{47} \)) at several points in order to obtain numerical second derivatives of the total energy. These forces are evaluated using highly converged wave functions at each ion displacement and so the force constant matrix generated should be an excellent numerical approximation to the force constant matrix, within the approximations of the \( \text{B3LYP functional} \) and computational conditions used. The phonon calculation in the \( P2/c \) unit cell was repeated several times under different computational conditions and the unstable mode was present in each case. The instability in the \( P2/c \) structure is likely to be caused either by the \( \text{B3LYP functional} \) or the \( P2/c \) approximation to the full \( Cc \) unit cell found in experiment\(^{3,26} \). The \( Cc \) structure is obtained from the \( P2/c \) structure by doubling the unit cell along the \( a \) and \( b \) crystallographic axes. A recent DFT + Hubbard U calculation, in which the crystal lattice was relaxed in both the \( P2/c \) and \( Cc \) unit cells, found a different charge order for the \( Cc \) unit cell in sites corresponding to \( B3/B4 \) chains\(^{19} \). The latter charge order is similar to the charge order pattern found by refinement of resonant x-ray diffraction studies of \( \text{Fe}_3\text{O}_4 \); the unstable mode whose ion displacements are concentrated on Fe and O sites in the B3 chains of the \( P2/c \) unit cell may be an indication that the charge order found in the \( P2/c \) unit cell is not the ground state in the \( Cc \) supercell.

IV. CONCLUSION

Vibrational modes of \( \text{Fe}_3\text{O}_4 \) in the cubic, high-temperature \( Fd\bar{3}m \) and monoclinic, low temperature \( P2/c \) unit cells have been computed using DFT-GGA and \( \text{B3LYP} \) hybrid DFT functionals, respectively. There is good agreement between IR and Raman active mode frequencies for the \( Fd\bar{3}m \) phase with a 30.9 cm\(^{-1}\) mean absolute difference between experimental mode frequencies and predicted frequencies. The IR conductivity for the \( P2/c \) phase was calculated using a Lorentz oscillator model and eigenvectors calculated using a \( \text{B3LYP} \) functional. When \( \text{B3LYP mode frequencies} \) are scaled down by 5% there is good agreement between peak positions in the LO model and experiment. Increases in IR linewidth from 24 to 39 and from 26 to 36 cm\(^{-1}\) is observed in experiment on cooling through \( T_V \)\(^{31} \). This may be explained by the appearance of a number of new IR active modes as the symmetry is broken on going from the \( Fd\bar{3}m \) to the \( P2/c \) structure.

There are major changes in the Raman spectrum on cooling through \( T_V \). Raman active mode densities at the \( \Gamma \) point of appropriate symmetry are compared to polarized Raman spectra. There is good agreement in distributions of mode frequencies for both \( \text{A}_g \) and \( \text{B}_g \) modes when compared to polarized Raman spectra in experimental XZ and XY geometries, except for the XY spectrum below 300 cm\(^{-1}\). In the \( Fd\bar{3}m \) structure the two most intense lines are found at 540 (\( T_{2g} \)) and at 670 cm\(^{-1} \) (\( A_g \)). In the \( P2/c \) structure each of these modes is replaced by 4 \( A_g \) and 4 \( B_g \) Raman active modes which are split in frequency by 50 or 100 cm\(^{-1}\). This splitting occurs because charge ordering, which accompanies the transition between the cubic \( Fd\bar{3}m \) and monoclinic \( P2/c \) structures, induces symmetry breaking in force constants on Fe octahedral \( B \) sites. A detailed comparison of Raman line positions and intensities from theory and experiment would provide a powerful probe of the Verwey transition.

Acknowledgments

The authors are grateful to David Tanner for helpful discussions and for use of IR data on magnetite reproduced from Ref. [31] in Fig. 4. CHP acknowledges discussions with Paul Attfield on x-ray and neutron scattering work in Ref. [3] and with Roberto Dovesi on choices of computational parameters. Computer time used in this work was provided by the Trinity Centre for High Performance Computing which is supported by the Irish Higher Education Authority and Science Foundation Ireland through the Irish National Development Plan. LVG acknowledges support by the National Science Foundation grant No. DMR-08-05-073, Research Corporation
Vibrational modes of Fe$_3$O$_4$ at the Γ point of the Brillouin zone were calculated using the Crystal package and the B3LYP hybrid functional. Vibrational frequencies of the magnetic insulator, andradite Ca$_3$Fe$_2$Si$_3$O$_{12}$, calculated using the Crystal package, have a mean absolute error less than 10 cm$^{-1}$ when compared to experiment. A study of the relative accuracies of HF, B3LYP, local density approximation (LDA) and Perdew-Burke-Enzerhof (PBE) functionals for calculating vibrational mode frequencies of α quartz at the Γ point found mean absolute errors of 44, 5.8, 17.5 and 21.0 cm$^{-1}$, and maximum absolute errors of 85.2, 22.1, 42.6 and 40.1 cm$^{-1}$, respectively. The mean absolute error in the phonon calculation on Fe$_3$O$_4$ presented here was 30.9 cm$^{-1}$ and the maximum absolute error was 86 cm$^{-1}$ for the $A_g$ mode. This breathing mode is predicted to lie at a very similar frequency by another DFT-GGA calculation, whereas frequencies predicted by B3LYP for equivalent modes in the $P2_1/c$ unit cell are much closer to the experimental value of 670 cm$^{-1}$. These larger errors likely reflect the more complex electronic structure of a narrow gap or metallic oxide compared with quartz, which is a wide gap insulator. Magnitudes of frequencies of modes which correspond to lattice translations were around 1 cm$^{-1}$.

The effect of lattice constant and weight of HF exchange in the functional on vibrational frequencies is illustrated in Fig. 10. There is a small downward shift in peaks in the conductivity spectrum when lattice constants are relaxed and there are only minor changes in the shape of the spectrum. Increasing the weight of HF exchange in the functional shifts frequencies upwards by about 10%.

All electron Gaussian orbital basis sets used in this work are: an Fe 20s12p6d basis contracted to 5s4p2d, previously used to study hematite and a 14s6p basis contracted to 4s3p, previously used to study NiO with a $d$ polarization function with exponent 0.5. Integration over the Brillouin zone was done using a 6x6x6 Monkhorst-Pack net and the densest standard grid for integration in the DFT part of the functional in the Crystal package were used. Fig. 1 was produced using the XCrySDen visualization package and phonon eigenvectors were drawn using the Moldawn package.

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{conductivity_graph.png}
\caption{(Color online) Conductivity of Fe$_3$O$_4$ parallel to the $c$ axis computed using a B3LYP functional and the LO model in Eq. 1 with lattice constants fixed at experimental values or fully relaxed and with weights of HF exchange, $A = 0.2$ or 0.3.}
\end{figure}