Enhanced Magnetization in $V_xFe_{3-x}O_4$ Nanoparticles

V. L. Pool^{a,1}, M. T. Kleb^{b,c}, C. L. Chorney^b, E. Arenholz^d, and Y.U. Idzerda^{a}*

^aDept. of Physics; Montana State University; Bozeman, MT 59715

^bDept. of Chemistry; Montana Tech; Butte, MT 59701

^cCtr. Advanced Supramolecular and Nanoscale Systems; Montana Tech; Butte, MT 59701

^dAdvanced Light Source; Lawrence Berkeley Nat. Labs; Berkeley, CA 94720

KEYWORDS: Magnetic nanoparticles, magnetism, XMCD, XAS

*Corresponding author: Idzerda@montana.edu

¹Current Address: SLAC National Accelerator Laboratory, Menlo Park, CA 94025

ABSTRACT

Nanoparticles of $V_xFe_{3-x}O_4$ with up to 33% vanadium doping ($x=0$ to 1) and a 9 nm diameter are investigated in order to determine the site preference of the vanadium and the magnetic behavior of the nanoparticles. The iron and vanadium L_{23} -edge X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (MCD) spectra are used to identify that vanadium initially

substitutes into the tetrahedral iron site as V^{3+} and that the average iron moment is observed to increase with vanadium concentration up to 12.5% ($x=0.375$). When the vanadium incorporation exceeds 12.5%, the XAS and MCD show that the vanadium begins substituting as V^{2+} in the octahedral coordination. This coincides with a rapid reduction of the average moment to zero by 25% ($x=0.75$). The frequency-dependent alternating-current magnetic susceptibility (ACMS) displays a substantial increase in blocking temperature with vanadium concentration and indicated substantial variation in the strength of inter-particle interactions.

Introduction

The ferrimagnetic nature of the spinel Fe_3O_4 makes it an interesting host material for substitutional doping with transition metals because the dopant valence and substitution site dramatically influence the magnetic properties of this material. Spinels have 24 cation sites per unit cell. For Fe_3O_4 , there are 8 tetrahedral Fe^{3+} sites with $5 \mu_B$ moment per iron atom and 16 octahedral sites split evenly between Fe^{2+} and Fe^{3+} ions, each with an atomic moment of $4 \mu_B$ and $5 \mu_B$ respectively. The tetrahedral and octahedral sublattices are anti-aligned due to the indirect exchange interaction between the two sublattices. Since the net moment of the tetrahedral and octahedral sublattices are not equal, this generates a $32 \mu_B$ net moment per unit cell due to the 8 Fe^{2+} octahedral iron atoms each with an uncompensated moment of $4 \mu_B$, resulting in an average moment of only $1.33 \mu_B$ per iron atom.

As a result of this ferrimagnetic behavior, the net moment of the unit cell will vary depending on the substitutional site of the dopant ion. If a nonmagnetic dopant ion substitutes for an Fe atom in the octahedral position the total moment of the octahedral sublattice (which is the dominant moment within the unit cell) will be reduced resulting in a decreasing net moment of the unit cell.

In the case of the nonmagnetic dopant taking the place of the tetrahedral iron atom however, the moment would initially increase as the total moment of the oppositely aligned tetrahedral sublattice decreases. For a nonmagnetic dopant, the ferrimagnetic ordering of the material generated by the indirect exchange between the sublattices will eventually break down with sufficient dopant incorporation^{1,2}.

The availability of different valence states makes vanadium doping promising as a cathode material for lithium ion rechargeable batteries³, as a useful catalyst⁴, and in applications as optical switches and detectors⁵. Studies for vanadium doping into the bulk spinel found it to substitute into the octahedral coordination⁶⁻¹⁰. Ionic accommodation¹¹ and energy minimization within crystal field calculations¹² as a function of dopant type both identify vanadium as a dopant with a marginal octahedral site preference. For nanoparticles, both accommodation arguments and orbital overlaps may be altered sufficiently to change the vanadium ion substitution site preference. An example of this is found in manganese-doped Fe₃O₄ nanoparticles encapsulated inside apo-ferritin protein cages¹³. The manganese was found to occupy the octahedral site and the magnetism of the nanoparticles (as measured by XMCD) was notably reduced with even the smallest incorporation of manganese. This nanoparticle behavior is distinct from the bulk behavior since the Mn in the protein encapsulated nanoparticle is found to substitute into the octahedral site with an oxidation of 2+ when in numerous bulk studies it is shown to prefer the tetrahedral coordination in that same ionization state^{6,12}. In another study done on gallium-doped Fe₃O₄ particles¹⁴ the gallium was found to substitute into the tetrahedral site and the average moment per iron atom increased to double its magnitude at its maximum value before dropping to zero by 33% incorporation, consistent with the expected behavior of a nonmagnetic dopant initially substituting for the tetrahedral coordinated iron.

Experimental Procedure

Nanoparticles of $V_xFe_{3-x}O_4$ with up to 33% vanadium doping ($x=0$ to 1) were synthesized by mixing appropriate ratios of solutions of 0.5 mmol $V(acac)_3$ and $Fe(acac)_3$, 1,2-hexadecanediol with benzyl ether, oleic acid (1.5 mmol), and oleylamine (1.5 mmol) under evacuated conditions. The mixture was gradually heated to 200°C and allowed to anneal for 24 hours. The reaction mixture was then cooled to room temperature, and the particles were precipitated in ethanol, centrifuged, and dried. Transmission electron microscopy (TEM) showed that these nanoparticles had a size distribution of 9 ± 2 nm.

X-ray absorption spectroscopy (XAS) and X-ray Magnetic Circular Dichroism (MCD) measurements were performed in electron yield mode at beamline 6.3.1 of the Advanced Light Source of the Lawrence Berkeley National Laboratories. Nanoparticles were prepared by drying the liquid suspension of the particles on formvar coated TEM grids. The MCD measurements were made with an alternating 0.5 T magnetic field at every energy point, sufficient to align the magnetic moment of the nanoparticles to be parallel or anti-parallel with the propagation direction of the circular polarized soft x-rays. The V and Fe L_{23} -edge and O K-edge XAS and the Fe L_{23} -edge MCD spectra were compared to reference standards and with molecular-orbital calculations. The V L_3 -edge peak energies are referenced to 515.9 eV by comparing the Ti L_3 -edge peak energies of a subsequently measured TiO_2 powder standard with the literature value for Ti from de Groot *et al.*¹⁵ This energy calibration automatically references the nearby O K-edge, which is collected along with the V-edge spectra.

Frequency-dependent alternating-current magnetic susceptibility (ACMS) measurements were accomplished using a Quantum Design Physical Properties Measurement System (PPMS) on dried samples of the nanoparticles with a distribution of frequencies ranging from 178 Hz-10,000 Hz to determine the frequency dependence of the blocking temperature of the nanoparticles.

Results and Discussion

To determine the valence of the substituting vanadium, area normalized XAS of the oxygen K-edge and vanadium L_{23} -edge were measured. The vanadium results (bottom panel of Figure 1) can be compared to the variation in the vanadium spectra in reference powders and with reference materials reported in the literature ^{16, 17} to associate various peaks in these spectra with vanadium valence. In the L_3 peak, the higher energy peak at 515.9 eV is strictly associated with the V^{3+} valence and the lower energy shoulder is associated with V^{2+} . This peak association with vanadium valence is used to determine that the vanadium initially substitutes as V^{3+} up to 12.5% ($x=0.375$) but as the concentration rises, vanadium additionally substitutes as V^{2+} , as evidenced by the growth of the lower binding energy peak in the vanadium XAS and the shift in energy of a lower energy peak in the oxygen K-edge spectra (top panel of Figure 1). Peak fitting of the vanadium spectra allows for a quantitative determination of the V^{2+} -to- V^{3+} compositional ratio (shown as an inset in Figure 1). If the extracted peak heights are proportional to the relative valence occupation, then only 13% of the vanadium resides in the V^{2+} state at $x=1$ vanadium doping levels.

As vanadium is substituted into the Fe-oxide spinel structure, the average moment of the iron atom, as determined by the Fe L_3 MCD intensity, is observed to initially increase over the same doping range where the V^{3+} substitution was identified (the red data points in Figure 2). Furthermore, the evolution of the Fe L_3 MCD spectra with vanadium concentration indicates that Fe is initially vacating the tetrahedral site due to substitution of the vanadium, as evidenced by the reduction in relative intensity of the middle peak of the MCD (Figure 3 displays the Fe L_3 MCD after normalization to the first negative peak for comparative purposes).¹⁸ This initial reduction and the overall increase in the Fe MCD strength is strong evidence that the vanadium first substitutes into the tetrahedral site of the spinel structure. At higher vanadium doping levels, the total Fe L_3 MCD intensity decreases and the relative peak intensities show that the Fe ions are now being removed from the octahedral sites as the vanadium valence shifts to V^{2+} and substitutes into the octahedral site.

This variation can be compared to four simple models for the average Fe moment with dopant substitution. The moment is determined by calculating the difference in the total moment the two anti-aligned sublattices as dopant ions are substituted for iron in either the octahedral or tetrahedral site with either a 2+ or 3+ valence (the remaining iron ionization values may change to maintain overall charge neutrality, affecting the atomic moment). Since MCD is an element-specific probe of the atomic moment, the total calculated moment must be normalized by the number of remaining iron atoms for comparison to the Fe MCD intensity. The results of this calculation are displayed as the lines in Figure 2 plotted along with the iron MCD intensities extracted for the vanadium-doped nanoparticles. For comparison, the values for the Fe MCD intensity for gallium-doped nanoparticles produced in an identical synthesis process are also shown (reported in previous work¹⁴). The iron MCD of both the vanadium and the gallium track with this model closely, in the low dopant concentration region, where it should approximate the magnetic behavior well.

As the concentration of vanadium increases beyond 12.5% (where the vanadium begins to substitute as V^{2+}), the average iron moment falls. The relative strength of the first dip in the iron XMCD spectra is also reduced for this doping level, indicating that the average moment of the Fe^{2+} ion in the octahedral position is smaller. This would occur if the additional vanadium now substitutes into the octahedral position (thereby reducing the overall iron moment).

When seen in comparison to the gallium work in which the gallium was found to substitute as 3+ in the tetrahedral position¹⁴ (consistent with the behavior reported for this material in bulk studies), it is clear that the vanadium is initially incorporated in the same manner as the gallium (as a substitutional ion in the 3+ tetrahedral site, counter to the bulk studies). Once the vanadium concentration exceeds 12.5%, incorporation also occurs as V^{2+} in the octahedral site and may be evidence of a crystal relaxation as has been seen in previous work on nanoparticles¹³.

The XAS and XMCD spectra are useful for determining elemental electronic and magnetic structure but, as local probes, they are not useful for determining inter-particle interactions that can modify the macroscopic magnetic behavior. Frequency dependent ACMS is often used to determine anisotropy energies and demonstrate that nanoparticles are non-interacting by showing they obey a linear Neel-Arrhenius behavior that extrapolates to a reasonable attempt time^{19,20} of the order 10^{-9} - 10^{-12} sec (this serves as a definition for non-interacting, and under these criteria the interaction is considered to be sufficiently small to be ignored). The ACMS data for the V-doped nanoparticles display a typical peak in the real part of the magnetic susceptibility associated with a blocking temperature, T_B , shown to increase with increasing vanadium concentration (see Figure 4a). This increase is quite dramatic, for the 5% concentration the blocking temperatures range from 75K to 85K, but for nanoparticles with a 33% concentration the blocking temperatures were above room temperature and so were not measurable with the set up used. For those concentrations that had measurable blocking temperatures, a standard Néel-Arrhenius plot was derived, and the anisotropy energies were determined and displayed in Figure 4b. While the data fits a straight-line fairly well, suggesting a good match to the Arrhenius law given in Eq. (1), for all non-zero vanadium concentrations, the extrapolated attempt times, τ_0 , were far from realistic indicating that the particles can no longer be considered non-interacting, and instead must be treated as weakly interacting.

$$\tau = \tau_0 \exp\left(\frac{E_a}{k_B T_B}\right) \quad (1)$$

The fact that the particles are interacting is not surprising for this synthesis method and has been seen previously in our study of Ga-doped iron oxide particles¹⁴. Interestingly, particle-particle interactions are not observed for an alternate synthesis process, in which nanoparticles are encapsulated in protein shells, where the protein shell sufficiently separates the nanoparticles to eliminate these interactions as indicated by their reasonable attempt times²¹.

For weakly interacting nanoparticles, a more appropriate treatment is to analyze the frequency dependent ACMS data using the Volger-Fulcher law given in Eq. (2) where the interactions are represented by an effective interaction temperature T_0 which serves to correct the measured blocking temperature^{22, 23}.

$$\tau = \tau_0 \exp\left(\frac{E_a}{k_B(T_B - T_0)}\right) \quad (2)$$

Additional measurements at much higher frequencies like Mossbauer experiments (GHz) would illustrate this non-linearity and allow for a simultaneous fitting of the effective interaction temperature and the anisotropy energy. In the absence of an independent determination of this effective interaction temperature, pre-selecting the attempt time allows for a determination of both the anisotropy energy and T_0 . Employing a reasonable set of attempt times ranging from 10^{-9} - 10^{-12} sec, the resulting anisotropy energies determined from the Volger-Fulcher treatment are displayed in Figure 4c using an expanded scale. Regardless of what attempt time is used, the trend is an increasing anisotropy with vanadium concentration. Extracting the effective interaction temperature and normalizing it by the measured blocking temperature generates a figure-of-merit for the strength of the inter-particle interaction. This is done for each concentration with a preselected range of different attempt frequencies and is displayed in Figure 4d. The inter-particle interaction is similarly observed to increase with vanadium concentration, even in the region where the net iron moment is small.

While at first glance this appears to provide more reasonable values with more believable anisotropy energies, the T_0 values extracted from this method were quite high in comparison to the blocking temperatures as seen in Figure 4d. In strict terms, the Volger-Fulcher law is valid for small interactions where the smallness criteria is $T_0 \ll T_B$.²³ Attempts to extend this treatment to larger interactions through the generalization of either the Arrhenius treatment²⁴ or the Volger-Fulcher treatment²⁵, have been employed with limited successes. These more involved treatments raise

additional questions while maintaining the trend of increasing anisotropy energy with vanadium concentration.

Conclusions

Vanadium doped iron oxide nanoparticles with an average size of 9 nm were found to preferentially substitute into the tetrahedral site as V^{3+} up to 12.5% vanadium incorporation, resulting in a large increase in the net iron moment. Beyond 12.5% vanadium concentration, the preference changes and the vanadium no longer substitutes exclusively in the tetrahedral site as V^{3+} but additionally substitutes as V^{2+} in the octahedral coordination. At these concentrations, the net Fe moment falls rapidly, as would be expected if the indirect-exchange interactions within the two sublattices were weakened. The frequency-dependent ACMS results identify a strong correlation between the vanadium concentration and the anisotropy energy within the particle and demonstrate that these particles are interacting. The strength of the inter-particle interaction is determined to be strongly dependent on vanadium concentration identifying them as highly tunable in this regard.

ACKNOWLEDGMENT

This work is supported by the National Science Foundation (CBET-0709358). The Advanced Light Source is supported by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

REFERENCES

1. A. H. Morrish, *The Physical Principles of Magnetism*. (IEEE Press, New Yourk, 2001).
2. W. Gorter, Philips Res. Rep. 9, 351 (1954).
3. K. M. Abraham, J. L. Goldman and M. D. Dempsey, Journal of The Electrochemical Society 128 (12), 2493-2501 (1981).
4. X. Gao and I. E. Wachs, The Journal of Physical Chemistry B 104 (6), 1261-1268 (2000).
5. H. Jerominek, F. Picard and D. Vincent, Opt. Eng. 32, 2092 (1993).
6. C. Gleitzer, J. Goodenough, B. Hyde, M. O'Keeffe and U. Weser, in *Cation Ordering and Electron Transfer* (Springer Berlin / Heidelberg, 1985), Vol. 61, pp. 1-76.
7. J. B. Goodenough, *Magnetism and the Chemical Bond*. (Wiley, New York, 1966).
8. M. Wakihara, Y. Shimizu and T. Katsura, Journal of Solid State Chemistry 3 (4), 478-483 (1971).
9. M. J. Rossiter, Journal of Physics and Chemistry of Solids 26 (4), 775-779 (1965).
10. V. Nivoix and B. Gillot, Solid State Ionics 111 (1-2), 17-25 (1998).
11. R. J. Hill, J. R. Craig and G. V. Gibbs, Physics and Chemistry of Minerals 4 (4), 317-339 (1979).
12. A. Navrotsky and O. J. Kleppa, Journal of Inorganic and Nuclear Chemistry 29 (11), 2701-2714 (1967).
13. V. Pool, M. Klem, C. Jolley, E. A. Arenholz, T. Douglas, M. Young and Y. U. Idzerda, Journal of Applied Physics 107 (9), 09B517 (2010).

15. F. M. F. de Groot, J. C. Fuggle, B. T. Thole and G. A. Sawatzky, *Physical Review B* 42 (9), 5459 (1990).
16. R. Zimmermann, P. Steiner, R. Claessen, F. Reinert, S. Hufner, P. Blaha and P. Dufek, *Journal of Physics: Condensed Matter* 11 (7), 1657 (1999).
17. M. Abbate, H. Pen, M. T. Czyżyk, F. M. F. de Groot, J. C. Fuggle, Y. J. Ma, C. T. Chen, F. Sette, A. Fujimori, Y. Ueda and K. Kosuge, *Journal of Electron Spectroscopy and Related Phenomena* 62 (1-2), 185-195 (1993).
18. J. S. Kang, G. Kim, H. J. Lee, D. H. Kim, J. H. Shim, S. Lee, H. Lee, J. Y. Kim, B. H. Kim and B. I. Min, *Physical Review B* 77 (2008).
19. L. Néel, *Ann. Geophys.* 5, 99 (1949).
20. W. F. Brown, Jr., *Physical Review* 130 (5), 1677 (1963).
21. V. L. Pool, M. T. Klem, J. Holroyd, T. Harris, E. Arenholz, M. Young, T. Douglas and Y. U. Idzerda, *J. Appl. Phys.* 105 (7), 07B515 (2009).
22. M. Tadić, D. Marković, V. Spasojević, V. Kusigerski, M. Remškar, J. Pirnat and Z. Jagličić, *Journal of Alloys and Compounds* 441 (1-2), 291-296 (2007).
23. S. Shtrikman and E. P. Wolfart, *Phys. Lett. A* 85, 467 (1981).
24. K. Binder and A. P. Young, *Physical Review B* 29 (5), 2864 (1984).
25. C. Z. Andérico, J. F. Fernández and T. S. J. Streit, *Physical Review B* 26 (7), 3824 (1982).

FIGURE 1: (TOP) O K-edge XAS and (BOTTOM) vanadium L_{23} -edge XAS for 9 nm vanadium doped iron oxide nanoparticles. INSERT: Extracted V^{2+}/V^{3+} XAS ratio as a function of vanadium concentration.

FIGURE 2: Iron MCD intensity vs. vanadium concentration compared to previously measured gallium data and substitution models.

FIGURE 3: Iron L₃-edge MCD for vanadium concentrations of 0%, 5%, 10%, 20% and 33%. Inset: Variation of the tetrahedral coordinated Fe site.

FIGURE 4: Dependence on the vanadium concentration for the (a) blocking temperature, (b) extracted anisotropy energy from the Arrhenius law, (c) extracted anisotropy energy from the Volger-Folcher law with different values attempt times, and (d) extracted T_0 to T_B ratios.