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Electronic and Magnetic Structure Study of NiV_2O_4

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Abstract

Inspired by recent experiments and theoretical work on vanadium spinels, the least investigated vanadium spinel i.e. NiV_2O_4 has been explored theoretically in this work. The systems is found to have an optimized vanadium- vanadium distance of 2.94 Å, which is the same as the limit of itinerancy in vanadium spinels. This indicates that the system is sitting exactly at the border between metallic and insulating phase. The calculations show that there is no tetragonal distortion present in it and it would prefer normal spinel structure. The DFT calculations have been performed using GGA approximation.

Keywords: Spinels, DFT, GGA, Electronic Structure Calculations

1. Introduction

Vanadium spinels have been fascinating both the theoreticians and experimentalists for years because of their very unusual magnetic and orbital order. For example, MnV_2O_4 undergoes a magnetic phase transition at 53 K from collinear ferrimagnetic order to non-collinear magnetic order accompanied by a structural transition [1], while CoV_2O_4, without undergoing any structural transition, shows two magnetic transitions from paramagnetic to ferrimagnetic at 142 K and from collinear ferrimagnetic to non-collinear ferrimagnetic at 59 K [2, 3]. The vanadium spinels AV_2O_4 can be broadly divided into two categories: antiferromagnetic vanadium spinels, the ones where the A-site is occupied by a nonmagnetic ion e.g ZnV_2O_4, MgV_2O_4, CdV_2O_4, the other kind is ferrimagnetic vanadium spinels, where A-site is occupied by a magnetic ion e.g. MnV_2O_4, FeV_2O_4, CoV_2O_4. In this work the vanadium spinel NiV_2O_4 is studied theoretically, which should fall under the category of ferrimagnetic vanadium spinels as the A-site is occupied by a magnetic ion. To the best of our knowledge, there is no experimental data available on this spinel. So it would really be very interesting to study this compound theoretically and compare with the other such compounds (MnV_2O_4, FeV_2O_4, CoV_2O_4 etc.) in this series. In vanadium spinels, the magnetic interaction among the vanadium ions plays an important role in dictating their physical properties. In the ferrimagnetic vanadium spinels, the vanadium- vanadium distance (d_{V-V}) decreases in the order $MnV_2O_4 > FeV_2O_4 > CoV_2O_4$ making MnV_2O_4 the most insulating one and CoV_2O_4 the most conducting among the known ferrimagnetic vanadium spinels [4,5]. Among the ferrimagnetic vanadium spinels, the distance d_{V-V} decreases as one goes from left to right in the periodic table, i.e. d_{V-V} decreases on going from Mn to Fe to Co while the corresponding magnetic transition temperature increases. Thus we can expect the d_{V-V} for the spinel NiV_2O_4 to be less than that for CoV_2O_4, and it may as well be equal to or less than the limit of itinerancy. Thus NiV_2O_4 is likely to be more conducting in nature than CoV_2O_4. Noting that the electrical transport in CoV_2O_4 differs from MnV_2O_4 and FeV_2O_4 [2], one can anticipate a very different electrical transport behavior in case of NiV_2O_4. The vanadium spinels usually show a structural transition to tetragonal structure by reducing the symmetry and the c/a ratio increases as one moves from MnV_2O_4 to CoV_2O_4 (c/a = 1), thus it would be interesting to find out what value of c/a does NiV_2O_4 support, is it > or < or = 1? The NiV_2O_4 spinel has two magnetic ions Ni^{2+} with spin configuration $e_g^4t_{2g}^4$ and V^{3+} with spin

configuration $e_g^0 t_{2g}^2$, which makes both of the ions orbitally active. Hence NiV_2O_4 makes an interesting case study. Some of these issues have been addressed using the first-principle DFT calculations in this work. [1-6]

2. Methodology

The electronic structure calculations have been performed through full potential linearized augmented plane wave method as implemented in WIEN2k code [6, 7]. As there is no experimental data available for this compound, so start calculations an initial guess to the lattice parameters and atomic positions is taken from the experimental structural data of other spinels. The structure has been then optimized within two different exchange correlation functionals: local spin density approximation (LSDA) as well as Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) [8-10]. Typically all the vanadium spinels have normal spinel structure with cubic unit cell (space group $Fd\underline{3}m$ (227)) at a high temperature. To begin with the normal cubic spinel structure was chosen for NiV_2O_4 and the chosen lattice constants were a = b = c = 8.40 Å for the calculations. For the atomic positions the ideal spinel arrangement was taken into account i.e. Ni cation at (3/8,3/8,3/8), V cation at (0,0,0) and O anion at (1/4,1/4,1/4), which forms an ideal normal spinel. The muffin-tin radii for Ni, V and O were set to 1.97, 1.98 and 1.68 Å, respectively. 50 k points were taken in the irreducible wedge of the Brillouin zone. Optimizing the structure within two exchange correlation functionals: LSDA and GGA. It was found that GGA gives reasonable results. So the further calculations were carried out for NiV_2O_4 within GGA. To ascertain the trends obtained with WIEN2k using LSDA and GGA, the structure was optimized using VASP [9,10] as well within GGA and LDA approximation. The results show the same trend with the VASP calculations as with WIEN2. The further calculations were proceeded within GGA approximation using WIEN2k to explore NiV_2O_4 further.

3.Results and Discussions

Fig. 1 shows the variation of total energy per unit cell w.r.t. unit cell volume for nonmagnetic (NM), ferrimagnetic (FIM) and ferromagnetic (FM) ordering of Ni and V spins. The ferrimagnetic arrangement gives the minimum energy configuration at the optimized volume of the cubic unit cell as 973.366 $Å^3$ (a = b = c = 8.325 Å) with d_{V-V} = 2.942 Å, which is equal to the limit of inteneracy [5]. Hence this system is indeed sitting exactly at the border of metal to insulator transition and hence makes a very interesting study. Fig. 2 shows the optimized unit cell of NiV_2O_4, depicting NiO_4 tetrahedra and VO_6 octahedra in two different colors.

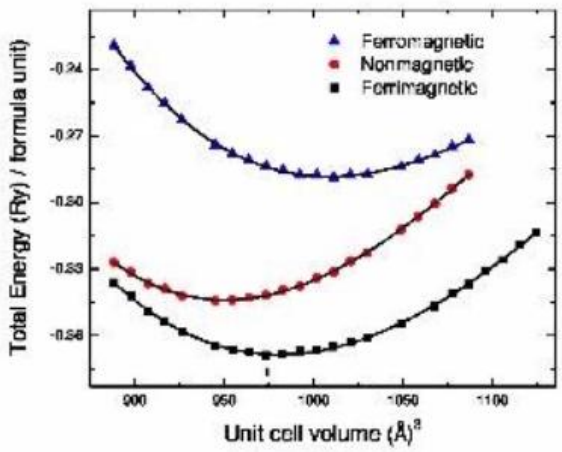

Fig.1. Total Energy vs. conventional cubic unit cell volume of NiV_2O_4 within GGA. Base value -7441 Ry is to be added to the total energy. Vertical line marks the equilibrium value for the energetically favored FIM state.

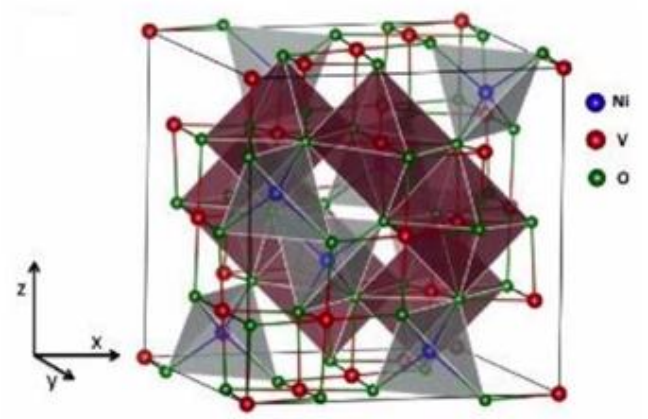

Fig.2. The cubic spinel unit cell of NiV_2O_4. Red (Grey) oxygen octahedra (tetrahedra) are around V (Ni) ions.

Fig. 3 presents the c/a ratio vs. total energy for NiV_2O_4. It can be easily seen that the cubic unit cell is more stable than the tetragonal unit cell for all the values of c/a, which implies that, similar to the case of CoV_2O_4, there should be no structural transition to tetragonal structure in NiV_2O_4 at low temperature.

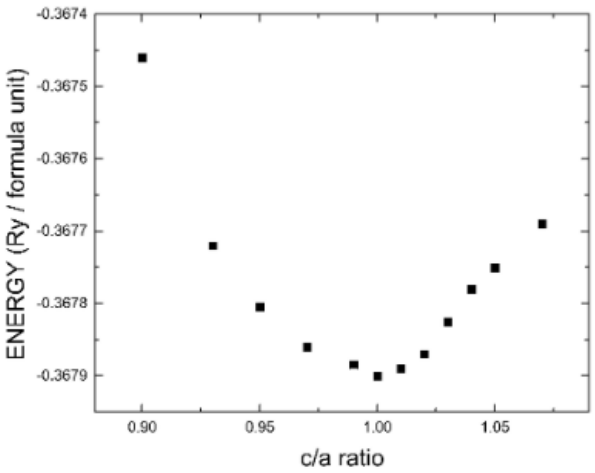

Fig.3. Total Energy vs. c/a value for NiV2O4 within GGA. The base value for total energy is -7441 Ry.

Further different magnetic arrangements for NiV_2O_4 have been studied within GGA. The total energy difference of various magnetic structures is given in Table 1. It is evident that Neel-type ferromagnetic (FIM) order is energetically the most favoured one.

Table.1. Energy difference ΔE, in Ry per formula unit, of various magnetic structures w.r.t ferromagnetic (FIM) structure.

Magnetic Structure	⊿E
E_{NM} - E_{FM}	0.0266
E_{FM} - E_{FIM}	0.0846
E_{AF} - E_{FIM}	0.0169

Conclusions

Using first-principle density functional theory calculations, we have proposed a possible crystal structure for NiV_2O_4 spinel for which no experimental data is available in literature. We have investigated NiV_2O_4 in detail and ruled out the possibility of any tetragonal distortion in the crystal structure. Through detailed electronic-structure calculation, Neel-type ferromagnetic (FIM) order has been found to be energetically more favorable. This system appears to be more itinerant than CoV_2O_4. This observation is consistent with our observation of V-V distance to be exactly 2.94 Å.

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