Two inequivalent sublattices and orbital ordering in MnV$_2$O$_4$ by $^{51}$V NMR

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We report detailed $^{51}$V NMR spectra in a single crystal of MnV$_2$O$_4$. The vanadium spectrum reveals two peaks in the orbitally ordered state, which arise from different internal hyperfine fields at two different V sublattices. These internal fields evolve smoothly with externally applied field, and show no change in structure that would suggest a change of the orbital ordering. The result is consistent with the orbital ordering model recently proposed by Sarkar et al. [Phys. Rev. Lett. 102, 216405 (2009)] in which the same orbital that is a mixture of $t_{2g}$ orbitals rotates by about 45$^\circ$ alternately within and between orbital chains in the $I4_1/a$ tetragonal space group.

Competition between spin interactions and orbital degeneracy is a key factor in determining the ground state magnetic and lattice structure of transition metal oxides, and gives rise to a rich spectrum of phase transitions in magnetic insulators. Recently, vanadium oxide spinels of the form AV$_2$O$_4$ have attracted interest, in which A is a divalent transition element that is either non-magnetic (Mg, Zn, Cd) or magnetic (Mn). The intriguing physics of the vanadate compounds arises from the geometrical spin frustration of the triply degenerate $t_{2g}$ orbitals of V$^{3+}$ ($3d^3$, $S = 1$) in the spinel structure. The V ions sit at the vertices of corner-sharing tetrahedra, and experience a magnetic exchange interaction with nearest neighbor V spins. In the process of relieving spin frustration, the vanadates typically undergo two consecutive phase transitions. First, a structural distortion splits the $t_{2g}$ levels into a low-lying $xy$ orbital and a higher doublet ($yz$, $zx$) at a temperature $T_S$. This structural phase transition is accompanied by long-range orbital ordering of the V orbitals, since Hund’s rules imply that a single electron occupies the excited doublet and orbital exchange interactions lift this degeneracy. If the A site is non-magnetic, then the V spins order antiferromagnetically at a lower temperature $T_N < T_S$.

When the A site is magnetic, novel features emerge that are distinct from the other vanadates. In particular, for Mn$^{2+}$ ($3d^{5}$) a ferrimagnetic (FEM) transition occurs before the structural transition ($T_S < T_N$). The combination of strong ferromagnetic Mn-Mn couplings, antiferromagnetic (AFM) Mn-V couplings, and AFM V-V couplings leads to a collinear FEM spin configuration at $T_N \sim 56$ K. This collinear state retains the orbital degeneracy, but is unstable so that upon further cooling the V spins become non-collinear below the structural transition at $T_S = 53$ K. Once again, long range orbital order of the V $d$ orbitals emerges in concert with structural distortion. However, the nature of the orbital symmetry remains poorly understood and continues to be debated theoretically in the literature. Experimentally, Adachi et al. proposed the ferro-orbital ordering in the $I4_1/amd$ tetragonal symmetry, but later x-ray and neutron experiments on single crystals claimed that the $I4_1/a$ space group was present with antiferro-orbital ordering in which $yz$ and $zx$ orbitals alternate along the $c$ axis. Although $I4_1/a$ space group allows only antiferro-orbital order due to the symmetry consideration, Chung et al. pointed out that the large exchange coupling along $c$ determined by neutron scattering is contradictory with the simple antiferro-orbital ordering. In fact, taking into account the staggered trigonal distortion, recent first principles calculations proposed a new orbital ordering in which the same orbital forms “anti-ferro” orbital order by rotating its direction by $\sim 45^\circ$ alternately within and between orbital chains, while maintaining $I4_1/a$ symmetry. The newly proposed orbital ordering model reconciles the contradicting experimental results and, indeed, is in good agreement with our NMR results. The three proposed orbital ordering models are schematically drawn in Fig. 1.

In order to investigate the orbital and magnetic order microscopically, we have carried out $^{51}$V nuclear magnetic resonance (NMR) as a function of field ($H$) and temperature ($T$) within the FEM state. In zero field, the $^{51}$V nuclear spins levels are split by an internal hyperfine field from the ordered Mn and V moments. The field dependence of the resonance reveals the non-collinear nature of the ordered moments. Single ferrimagnetic domain is formed above $H_c \sim 0.3$ T, while the orbital ordering is intact up to 13 T.

$^{51}$V NMR spectra were obtained on a single crystal of MnV$_2$O$_4$ between 4 and 35 K in zero field and in external fields up to 13 T. The preparation of the single crystal of MnV$_2$O$_4$ has been described in detail in Ref. 8. The spectra were obtained by integrating averaged spin echo signals as the frequency was swept through the resonance line. The V resonance in the single crystal (SC) is close to 285 MHz as we found in previous measurement of a polycrystal (PC) sample. However, the spectrum in the SC is narrower than in the PC and reveals two sharp features, whereas the PC sample is significantly broader with poorly resolved features (Fig. 2). These differences are consistent with recent x-ray diffraction and magnetization measurements as well as specific heat data, which show evidence of an impurity cubic phase result-
dered state. In this case, the splitting can be written as

\[ \nu = \nu_{Q} + \nu_{C} \]

ond order quadrupolar contribution in the orbitally or-

the two well resolved peaks might arise from the sec-

hyperfine field at the V.

A priori

I

orbital order in

H

cubic phase remained in SC sample.


\[ H = H_{F} + H_{l} + H_{d} \]

\[ H_{\text{hf}}^{\text{trans}} = \sum_{i} A_{i} S_{i} + \sum_{j} B_{j} S_{\text{Mn}i} \]

\[ \nu_{Q} = \gamma \nu_{C}/a \]

\[ \nu_{C} \]

\[ \nu_{Q} = A \gamma \nu_{C}/a \]

\[ \gamma = \gamma_{N}H_{\text{hf}} \]

\[ \nu_{C} = \gamma_{N}H_{\text{hf}} \]

\[ \gamma_{N} \]

\[ \nu_{C} \]

\[ \gamma_{N} \]

\[ \nu_{Q} = \gamma_{N}H_{\text{hf}} \]

\[ \nu_{C} \]

\[ \gamma_{N} \]

\[ \nu_{Q} = \gamma_{N}H_{\text{hf}} \]

\[ \nu_{C} \]

\[ \gamma_{N} \]

\[ \nu_{Q} = \gamma_{N}H_{\text{hf}} \]

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\[ \nu_{Q} = \gamma_{N}H_{\text{hf}} \]

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\[ \nu_{Q} = \gamma_{N}H_{\text{hf}} \]

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\[ \nu_{Q} = \gamma_{N}H_{\text{hf}} \]

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\[ \gamma_{N} \]

\[ \nu_{Q} = \gamma_{N}H_{\text{hf}} \]

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\[ \nu_{Q} = \gamma_{N}H_{\text{hf}} \]

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\[ \nu_{Q} = \gamma_{N}H_{\text{hf}} \]

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\[ \gamma_{N} \]

\[ \nu_{Q} = \gamma_{N}H_{\text{hf}} \]

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\[ \gamma_{N} \]

\[ \nu_{Q} = \gamma_{N}H_{\text{hf}} \]

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\[ \nu_{Q} = \gamma_{N}H_{\text{hf}} \]

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\[ \gamma_{N} \]

\[ \nu_{Q} = \gamma_{N}H_{\text{hf}} \]

\[ \nu_{C} \]

\[ \gamma_{N} \]

\[ \nu_{Q} = \gamma_{N}H_{\text{hf}} \]

\[ \nu_{C} \]

\[ \gamma_{N} \]
$I_{41}/a$ tetragonal symmetry because the V-V and Mn-V transferred hyperfine fields become different for two V sublattices depending on the orbital overlap between V-V and/or V-Mn via oxygen 2p orbitals [see Fig. 1(c)].

The two differentiated V sites appear to be robust against the variation of temperature and external field. As shown in Fig. 3 with increasing $T$, the spectrum shifts to lower frequencies, while retaining the same shape. Since $H_{hf}$ is proportional to the sublattice magnetization, we expect $\nu(T)$ to follow Bloch’s $T^{3/2}$ law at $T \ll T_N$. If there is an energy gap, $E_g$, in the spin wave excitation spectrum, $\nu(T)$ at sufficiently low $T$ is given by:

$$\nu(T) = \nu(0) \left[ 1 - \frac{a T^{3/2}}{E_g} e^{-E_g/T} \right],$$

where $a$ is a fitting parameter. The dotted lines in Fig. 3 are fits to this expression using $E_g = 17.4$ K. The fit is excellent for $T < 15$ K, but deviates above $T \gtrsim 0.25T_N$. Unfortunately, we lose the signal near 30 K due to short spin-spin relaxation rates, $1/T_2$, which increase as thermal fluctuations set in near the phase transition at $T_N = 56$ K.

We now turn to the external field dependence of the spectrum. Figure 3 shows the two peaks as a function of $H$ at 7 K. The initial slope of $\nu(H)$ vs. $H$ is zero as seen in the inset of Fig. 3. With increasing $H$, the slope increases gradually and reaches a fixed value above $H_c = 0.3$ T. This behavior indicates the existence of the FEM domain structure in zero field and its alignment along the external field $H$, forming a single domain above $H_c$. This is also consistent with the magnetization $M$ in field that is saturated to 3.2 $\mu_B$ as expected from the non-collinear spin structure.

![FIG. 3](image-url) (Color online) Temperature dependence of $^{51}$V spectrum in zero field. A Boltzmann correction by multiplying $T$ was made. The signal becomes weak rapidly with increasing $T$ and disappears above 35 K due to the shortening of $T_2$ associated with thermal fluctuation. Dotted lines are Eq. (3), implying that the spin wave theory is applicable at low $T$ region. Seemingly different $T$ dependence of relative intensities between two peaks is ascribed to the impurity cubic phase in which resonance frequencies are almost $T$ independent.

![FIG. 4](image-url) (Color online) External field dependence of resonance frequencies of two peaks at 7 K. Low field data are enlarged in inset. Zero slope at $H = 0$ indicates the existence of domain structure. Excellent fit above 0.3 T to 13 T with Eq. (4) was obtained with the fixed set of parameters (see text), indicating the formation of single domain above 0.3 T, and the robust spin structure up to 13 T. Inset shows the magnetization $M$ in field along [110] direction at the same $T$. $M$ is saturated to 3.2 $\mu_B$ as expected from the non-collinear spin structure.

The resonance frequency of the V is given by the net vector sum of the hyperfine and external fields at the nucleus:

$$\nu(H) = \gamma_N |H_{hf} + H| = \gamma_N \sqrt{H_{hf}^2 + H^2 + 2H_{hf}H \cos \theta},$$

where $\theta$ is the angle between $H_{hf}$ and $H$. This equation is plotted in Fig. 4 as a solid line, and clearly fits both peaks up to 13 T with the two parameters $H_{hf}$ and $\theta$ for each peak. We find that the fields and angles are 24.94 T with $\theta = 27.5^\circ$ and 25.23 T with $\theta = 28.8^\circ$. Since Mn$^{2+}$ is an orbital singlet ion ($3d^5$, $L = 0$), the Mn$^{2+}$ moment can be easily aligned along $H$ due to its large moment (4.2 $\mu_B$) and the essentially isotropic susceptibility. Then the Mn-V and V-V exchange interactions maintain the non-collinear FEM spin structure, which is depicted in the inset of Fig. 4. The excellent fits of data
to Eq. (4) indicate that the non-collinear spin structure remains robust up to 13 T. We emphasize that the different angles and hyperfine fields at two V sites are inconsistent with either simple antiferro- or ferro-orbital ordering because the V site are equivalent in both cases. Again, however, “antiferro” orbital chains formed by rotating orbitals with respect to each other is compatible with the two inequivalent V sites because the hyperfine fields at $^{51}$V nuclei can vary depending on the direction of the orbitals and/or on different overlaps of the on-site orbital with surrounding V d or O 2p orbitals.

We note, however, that the angles we obtain ($\sim 28^\circ$) differ significantly from those measured by neutron scattering ($\sim 65^\circ$). This result suggests that either (i) the orientation of the ordered spins changes in field, or (ii) $\mathbf{H}_{hf}$ is not coincident with the direction of the ordered V moments. Case (i) is possible if the delicate balance of exchange fields that gives rise to the particular FEM structure in zero field is modified by the presence of an external field. However, case (i) seems unlikely because the magnetization data at 7 K shows the saturation moment of about 3.2 $\mu_B$ (inset of Fig. 4), which is very close to the expected value of 3.1 $\mu_B$ from the given moments and the angle of $\sim 65^\circ$. Therefore, the large tilted angles of $\sim 35^\circ$ between $-\mathbf{S}$ and $\mathbf{H}_{hf}$ requires that the on-site orbital and dipolar terms be the same order as the isotropic Fermi contact term that is parallel to $-\mathbf{S}$. For the $V^{3+}$ ion, we can estimate the Fermi term $H_F \sim -28$ T. The anisotropic dipolar term can be estimated from the relation $H_d = 4/7\langle r^{-3}\rangle\mu_B = 2/7 \times 125\langle r^{-3}\rangle_a.u.$ kG.

Using $\langle r^{-3}\rangle_a.u. = 3.217_{18}$, $H_d \sim 11.4$ T. For the orbital term, the magnitude of $H_l$ could be approximated as $125\langle r^{-3}\rangle_a.u. = 40$ T for fully unquenched angular momentum. Taking into account the quenching, $H_l$ is expected to be the same order as the dipolar term, and is not necessary to be parallel to $H_F$, resulting in the total hyperfine field that is quite off the direction of the ordered moment. In this sense, the large tilted angle of $\mathbf{H}_{hf}$ could be understood as a consequence of the complex orbital ordering in the orbital triplet ground state of $V^{3+}$ ion, since the angular momentum is quenched in the perfect antiferro orbital ordering.

In conclusion, our $^{51}$V NMR study on a single crystal of MnV$_2$O$_4$ reveals the two inequivalent V sublattices that imply a complicated orbital ordering pattern in the $I4_1/a$ symmetry. Although we cannot determine a specific orbital ordering solely by NMR, our data put a strong constraint on the possible orbital ordering models. We find that the model proposed by Sarkar et al. is quite promising being compatible with our data. Also we have shown that the orbital ordering and the non-collinear spin structure are robust up to 13 T.

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