Magnetic excitations and anomalous spin-wave broadening in multiferroic FeV2O4

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Abstract
We report on the different roles of two orbital-active Fe2+ at the A site and V3+ at the B site in the magnetic excitations and on the anomalous spin-wave broadening in FeV2O4. FeV2O4 exhibits three structural transitions and successive paramagnetic (PM)–collinear ferrimagnetic (CFI)–noncollinear ferrimagnetic (NCFI)/ferroelectric transitions. The high-temperature tetragonal/PM–orthorhombic/CFI transition is accompanied by the appearance of a large energy gap in the magnetic excitations due to strong spin-orbit-coupling-induced anisotropy at the Fe2+ site. While there is no measurable increase in the energy gap from the orbital ordering of V3+ at the orthorhombic/CFI–tetragonal/NCFI transition, anomalous spin-wave broadening is observed in the orthorhombic/CFI state due to V3+ spin fluctuations at the B site. The spin-wave broadening is also observed at the zone boundary without softening in the NCFI/ferroelectric phase, which is discussed in terms of magnon-phonon coupling. Our study also indicates that the Fe2+ spins without the frustration at the A site may not play an important role in inducing ferroelectricity in the tetragonal/NCFI phase of FeV2O4.

Keywords
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Comments

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Magnetic excitations and anomalous spin-wave broadening in multiferroic FeV$_2$O$_4$

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We report on the different roles of two orbital-active Fe$^{2+}$ at the A site and V$^{3+}$ at the B site in the magnetic excitations and on the anomalous spin-wave broadening in FeV$_2$O$_4$. FeV$_2$O$_4$ exhibits three structural transitions and successive paramagnetic (PM)–collinear ferrimagnetic (CFI)–noncollinear ferrimagnetic (NCFI)/ferroelectric transitions. The high-temperature tetragonal/PM–orthorhombic/CFI transition is accompanied by the appearance of a large energy gap in the magnetic excitations due to strong spin-orbit-coupling-induced anisotropy at the Fe$^{2+}$ site. While there is no measurable increase in the energy gap from the orbital ordering of V$^{3+}$ at the orthorhombic/CFI–tetragonal/NCFI transition, anomalous spin-wave broadening is observed in the orthorhombic/CFI state due to V$^{3+}$ spin fluctuations at the B site. The spin-wave broadening is also observed at the zone boundary without softening in the NCFI/ferroelectric phase, which is discussed in terms of magnon-phonon coupling. Our study also indicates that the Fe$^{2+}$ spins without the frustration at the A site may not play an important role in inducing ferroelectricity in the tetragonal/NCFI phase of FeV$_2$O$_4$.

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I. INTRODUCTION

Understanding the orbital degrees of freedom and their coupling with spin and lattice degrees of freedom has emerged as a forefront topic in modern condensed-matter physics as these coupled degrees of freedom play a central role in inducing various novel phenomena [1]. Vanadium spinel oxides with formula AV$_2$O$_4$ [2] are ideal systems to study the orbital ordering (OO) by virtue of the fact that the 3$d^2$ high-spin configuration of V$^{3+}$ is accommodated in the triply degenerate $t_{2g}$ states rendering it with orbital degrees of freedom. For a nonmagnetic occupancy of the A site by a divalent ion such as Zn, Mg, and Cd [3], there is usually a structural transition from cubic to tetragonal, followed by a magnetic ordering at a lower temperature. Replacing A by a magnetic ion Mn$^{2+}$ in a 3$d^5$ high-spin configuration without orbital degrees of freedom leads to successive paramagnetic (PM)–collinear ferrimagnetic (CFI)–noncollinear ferrimagnetic (NCFI) magnetic transitions [4], while the latter one is accompanied by a similar cubic-tetragonal structural transition. In FeV$_2$O$_4$, the A-site Fe$^{2+}$ with a high-spin 3$d^6$ configuration and three electrons in the doubly degenerate $e$ states gives rise to orbital degrees of freedom [5,6]. FeV$_2$O$_4$ exhibits similar PM-CFI-NCFI magnetic transitions as in MnV$_2$O$_4$, but the competition or cooperation between two orbital-active Fe$^{2+}$ and V$^{3+}$ leads to three structural transitions, and a fourth one, albeit controversial [5,7,8]. Previous investigations have focused on the orbital ordering of V$^{3+}$ at the B site and its effect on the cubic-tetragonal transition and the magnetic excitations in AV$_2$O$_4$ (A = Zn, Mg, Cd, and Mn) [9–12]. However, the effect of the orbital ordering at the A site on the magnetic excitations in vanadium spinel oxides is not clear yet. FeV$_2$O$_4$ provides a good candidate to investigate the roles of orbital orderings not only on the B site, but also on the A site.

Distinct from perovskite oxides, relatively few spinel oxides such as CdV$_2$O$_4$ [13], ACr$_2$O$_4$ [14,15] (A = Co or Fe), were reported so far to display multiferroicity in the spinel oxide family. The reasons why the spinel oxides do not favor multiferroicity are still not clear. Recently, Zhang et al. discovered multiferroicity in FeV$_2$O$_4$ [7], where the ferroelectricity is not found in the collinear ferrimagnetic phase but only emerges in the noncollinear ferrimagnetic phase. It is of interest to compare the spin dynamics [16] in these two distinct magnetic phases, and also to figure out the source of the spin frustration in FeV$_2$O$_4$ since spin frustration is usually related to the appearance of the ferroelectricity in various noncollinear magnetic phases [17,18]. Motivated by the above issues, we studied high-quality FeV$_2$O$_4$ single crystal using a combination of magnetization measurements, and elastic and inelastic neutron-scattering techniques.

II. EXPERIMENTAL DETAILS

The FeV$_2$O$_4$ crystal was grown using the floating zone method. The dc susceptibility measurements were carried out on a Magnetic Property Measurement System (Quantum Design, SQUID). A big piece of crystal of the mass $\approx$1 g was cut for the elastic and inelastic neutron-scattering measurements that were conducted on the HB3 spectrometer (located at the High Flux Isotope Reactor at Oak Ridge National Laboratory, USA) with a fixed final energy (E = 14.7 meV).

III. RESULTS AND DISCUSSION

Figure 1(a) shows the splitting of the $q$ scans of the (400) structural Bragg peak in the cubic setting at several representative temperatures. The schematic pictures of distortion of the crystals and the definition of directions of crystalline axes
using different settings in different structures are summarized in Fig. 1(b). At 120 K, one (400) peak splits to (220)$_T$ and (400)$_T$ in the tetragonal notation, suggesting the $c$ axis of the cubic unit cell is compressed due to Jahn-Teller distortion of FeO$_4$ [5,7,8] driven by a ferroic Fe$^{2+}$ $3z^2$-$r^2$ OO [19] and the cubic structure transforms into a high-temperature (HT) tetragonal structure with $c_c < a_c$ ($a_c$ is the lattice constant in the cubic phase). As temperature further decreases to 92 K, one of the $a$ axes in the HT tetragonal phase is compressed [5], resulting in a structural transition to orthorhombic phase, which can be seen from the splitting of two peaks to three peaks (400)$_O$, (040)$_O$, and (004)$_O$. At 50 K, these three peaks evolve back to two peaks, indicating another structural transition to a low-temperature (LT) tetragonal phase. As opposed to the HT tetragonal phase, the peak position $q$ of (004)$_T$ is smaller than that of the (220)$_T$ peak in the LT tetragonal phase. Moreover, the peak intensity of the low-$q$ peak is weaker than that of the high-$q$ peak in the LT tetragonal phase. Thus, the LT tetragonal phase with $c > a$ is different from the HT tetragonal phase with $c < a$ and the tetragonal $c$ axes in these two tetragonal phases are perpendicular to each other in one unit cell. This indicates that the compressed axis ($b_O$ or $a_O$) in the orthorhombic phase, becomes equal to the $c_O$, and therefore, the orthorhombic phase evolves to a LT tetragonal phase and the third axis becomes the new $c$ axis in the tetragonal setting. Based on the above discussion, we notice that during the structural transformation from a HT tetragonal phase to a LT tetragonal phase in FeV$_2$O$_4$, the orthorhombic phase cannot be avoided. It should be noted that as shown in Fig. 1(a), no change is observed in the $q$ scans of the (400) structural Bragg peak between 50 and 15 K, excluding any structural transition at around 35 K as reported by Katsufuji et al. [5] but not by others [8,19].

The obtained lattice constants as a function of temperature shown in Fig. 2(a) indicate that there are three structural transitions: cubic-high-temperature (HT) tetragonal ($c < a$) at $T_3 = 140$ K, HT tetragonal-orthorhombic at $T_{N1} = 110$ K, and orthorhombic-LT tetragonal at $T_{N2} = 70$ K. It is worthwhile noting that $T_{N2}$ here, consistent with the value in Ref. [5], is a little higher than 56 K in polycrystalline samples [7,8], and 60 K [8] or 65 K [19] in single crystal form, reflecting strong suppression of the nonstoichiometry, i.e., $x \approx 0$ in the formulation (Fe$_{2+x}$)(Fe$_{3-x}$V$_{2-x}$)$_2$O$_4$ in our crystal as a lower value of $x$ causes an increase of $T_{N2}$ [20]. Thus, the investigation on the stoichiometric FeV$_2$O$_4$ crystal can minimize the effect of nonstoichiometry and reveal intrinsic magnetic excitations.

Figure 2(b) shows the temperature dependence of the dc susceptibility with zero-field cooling (ZFC) and field-cooled warming (FCW) modes in a magnetic field of 1000 Oe parallel to the [111]. Below $T_{N1}$, a rapid increase in the susceptibility is ascribed to the PM to CFI ordering where the Fe$^{2+}$ moments are parallel to the [001] and the V$^{3+}$ moments are antiparallel to the Fe$^{2+}$ moments via antiferromagnetic (AFM) coupling $J_{Fe-V}$ [7,8]. Another jump in the FC susceptibility below $T_{N2}$ results from CFI to NCFI transition due to the V$^{3+}$ canting [7,8] along any of the (111) directions [8]. The schematic CFI and NCFI magnetic structures projected on the $ac$ plane with the main magnetic interactions [7,8] are shown in Fig. 2(d). The inverse susceptibility shows a deviation below $T_S$, indicating a magnetoelastic coupling [5] at $T_S$. We note that FeCr$_2$O$_4$ with only orbital-active Fe$^{2+}$ exhibits similar PM cubic–PM tetragonal ($c < a$)–CFI orthorhombic transitions [21] without the lowest one at $T_{N2}$. Thus, the two transitions at $T_S$ and
$T_N_1$ in FeV$_2$O$_4$ are mainly ascribed to the involvement of orbital-active Fe$^{2+}$ [19]. The LT tetragonal phase with $c > a$ in FeV$_2$O$_4$ is unique in all the vanadium spinel oxides, suggesting both orbital-active Fe$^{2+}$ and V$^{3+}$ are necessary [5] to induce the third structural transition at $T_{N_2}$.

Figures 2(c) and 2(d) show the temperature dependence of integrated intensity and peak linewidth of the high-symmetry-cubic-forbidden (200) reflection in FeV$_2$O$_4$. The peak is present at all measured temperatures and exhibits anomalies at the three transitions. We note that the observed (200) is not due to $\lambda/2$ leakage as the PG filters remove this higher-order wavelength to better than one part in $3 \times 10^6$ as measured on the nuclear (220) Bragg peak and the forbidden (110) at 200 K. The observed (200) peak above $T_S$ at 200 K has a pure structural origin due to anisotropy of the local environment around the transition-metal atoms with no contribution from charge ordering or OO, as discussed in other spinels, such as AFe$_2$O$_4$ ($A = \text{Mn, Co, and Fe}$) [22]. Whereas weak anomalies at $T_S$ and $T_{N_1}$ in the intensities and linewidths are present, the (200) reflection with higher intensity and sharper peak below $T_{N_2}$ is mainly magnetic in origin, which confirms the occurrence of V$^{3+}$ spin canting as depicted in Fig. 2(d).

Constant-Q energy scans were measured at the zone center (220) at various temperatures and at various $Q$’s along [H H 0] at CFI (90 K) and NCFI (3.5 K) phases. As shown in Fig. 3(a), a clear energy gap $\approx 8$ meV at (220) in the low-$E$ region is observed at 3.5 K and the gap drops smoothly with increasing temperature. In the damped simple harmonic oscillator approximation [23–25], the neutron-scattering cross section is given by

$$\frac{d^2\sigma}{d\Omega dE}(\mathbf{q}, E) \propto \frac{A_q \Gamma E}{\{E^2 - \{E_0(q)\}^2\}^2 + \Gamma^2 E^2 (1 - e^{-E/kT})^{-1}},$$

where $A_q$ is $q$-dependent intensity, $\Gamma$ is the spin-wave damping factor and can also characterize the intrinsic magnon width, and $(1 - e^{-E/kT})^{-1}$ is the Bose factor. In the small-$q$ limit, the spin waves around (220) zone center can be approximately described by an anisotropic linear dispersion relation [4,23]:

$$E_0(q) = \sqrt{\Delta^2 + v_{iso}^2(q_x^2 + q_y^2)},$$

where $v$ is the spin-wave velocity and $\Delta$ is the energy gap. The constant-$Q$ energy scans have been fitted using Eqs. (1) and (2) after convolution with the instrumental resolution using the RESLIB program [26].

The temperature dependence of the energy gap at (220) zone center is shown in Fig. 3(b). Compared with the behavior of the energy gap in MnV$_2$O$_4$ [4] where only V has orbital degrees of freedom, FeV$_2$O$_4$ shows three main differences: (1) In FeV$_2$O$_4$ the gap emerges below $T_{N_1}$, whereas for MnV$_2$O$_4$ it only emerges below $T_{N_2}(=53$ K). (2) The gap in FeV$_2$O$_4$ is much higher. (3) No obvious increase in the energy gap ($\approx 1.5$ meV) as observed in MnV$_2$O$_4$ is found in FeV$_2$O$_4$ below $T_{N_2}$.

In the temperature range $T_{N_2} < T < T_{N_1}$ for both MnV$_2$O$_4$ and FeV$_2$O$_4$, the magnetic structures are similar without OO of V$^{3+}$ [19]. The main difference in this temperature region between these two systems is that Fe$^{2+}$ is orbital ordered whereas Mn$^{2+}$ is not. Thus, the appearance of an energy gap below $T_{N_1}$ in FeV$_2$O$_4$ is due to the involvement of Fe$^{2+}$ OO and not related to V$^{3+}$ ions. It has been shown that the sole PM-CFI magnetic transition without any OO cannot induce an energy gap below $T_{N_1}$ in MnV$_2$O$_4$ [4]. Furthermore, the sole ferroic Fe$^{2+}$ 3$\text{c}^2$-$\text{r}^2$ OO [19] does not induce the energy gap below $T_{N_1}$ since the OO is formed at a higher temperature $T_S$. Therefore, the spin-orbit-coupling-induced anisotropy at the A-site Fe$^{2+}$ is responsible for the appearance of the gap. High-resolution synchrotron x-ray measurements on FeV$_2$O$_4$ [19] have shown that there is a strong spin-orbit coupling at the A-site Fe$^{2+}$ and the CFI ordering below $T_{N_1}$ triggers the structural transition to orthorhombic with a lower symmetry via the spin-orbit coupling, similar to ACr$_2$O$_4$ ($A = \text{Fe and Cu}$) with only an orbital-active ion at the A site [21]. Compared with MnV$_2$O$_4$, the much higher energy gap in FeV$_2$O$_4$ results from stronger spin-orbit coupling at the Fe$^{2+}$ A site than that of the V$^{3+}$ B site in MnV$_2$O$_4$. The larger ordered moment of 4.0$\mu_B$ [8] of Fe$^{2+}$ below $T_{N_1}$ than that of the V ion ($1.3\mu_B$) in MnV$_2$O$_4$ also contributes to the higher gap. Below $T_{N_2}$, although spin ordering of V$^{3+}$ is similar and V$^{3+}$ becomes orbital ordered in both MnV$_2$O$_4$ and FeV$_2$O$_4$, the absence of a measurable increase in energy gap below $T_{N_2}$ in FeV$_2$O$_4$ implies nearly quenched orbital moments or a very weak SO coupling for the V$^{3+}$, consistent with soft x-ray magnetic circular dichroism experiments [27] and theoretical calculations [6].

To get further insight into the temperature evolution of the energy gap, we performed a least-square fit using power law $\Delta(T) \propto (T_{N_1} - T)^d$ and obtained an exponent $d \approx 0.75$ below $T_{N_1}$, similar to the value of $\approx 0.73$ in MnV$_2$O$_4$ below $T_{N_2}$ [4]. This indicates the energy gap induced by the anisotropy at the Fe$^{2+}$ site in FeV$_2$O$_4$ has similar temperature evolution and critical behavior as the energy gap due to the anisotropy at the V$^{3+}$ B site in MnV$_2$O$_4$. We also modeled the temperature dependence of the integrated intensity of Bragg peak (220) around $T_{N_1}$ and $T_{N_2}$ using $I(T) \propto (T_{N_1,N_2} - T)^{\beta d}$, yielding critical exponents $\beta_1 \approx 0.353$ at $T_{N_1}$ and $\beta_2 \approx 0.381$ at $T_{N_2}$.

FIG. 3. (Color online) (a) Constant-Q energy scans measured at the zone center (220) at various temperatures. The solid lines are fits using the model described in the text. (b) Temperature dependence of the energy gap, damping factor $\Gamma$, and (c) the integrated intensity of the (220) Bragg peak. The solid lines are fits to the data (see text for more details).
This indicates that FeV$_2$O$_4$ is close to the three-dimensional (3D) Heisenberg ($\beta = 0.36$) or 3D Ising ($\beta = 0.33$) models. These two critical exponents are similar to the values near $T_{N1}$ and $T_{N2}$ reported in MnV$_2$O$_4$ [4]. The comparison of $\beta_1$ with $d$ values below $T_{N1}$ in FeV$_2$O$_4$ indicates that the temperature dependence of the energy gap varies like the square of the staggered magnetization [4] once the CFI ordering sets in.

We emphasize that the spin-wave damping factor $\Gamma$ [see Fig. 3(b)] increases rapidly at $T_{N2}$. We also used the Lorentz function convoluted with the spectrometer resolution function to model constant-$\mathbf{Q}$ energy scans yielding FWHM values very close to $\Gamma$. Raising the temperature usually leads to a gradual spin-wave broadening but the clear anomaly at $T_{N2}$ excludes thermal effect only. We argue that the spin-wave broadening in $T_{N2} < T < T_{N1}$ originates from strong fluctuations of $V^{3+}$ spins on the $B$ site in the CFI phase prior to their true canting below $T_{N2}$. Such spin fluctuations of $V^{3+}$ affect the Fe spin waves and therefore lead to the anomalous spin-wave broadening in $T_{N2} < T < T_{N1}$.

Representative constant-$\mathbf{Q}$ $E$ scans at various $Q$'s along the [H H 0] in the NCFI/ferroelectric phase are shown in Fig. 4(a). The solid lines are the best fit using the model described above and the obtained spin-wave dispersions at the two different magnetic states are shown in Fig. 4(b). Similar to the behavior at the (220) zone center, $\Gamma$ at each fixed $\mathbf{Q}$ at 90 K is significantly larger than that at 3.5 K, as shown in the inset of Fig. 4(c). Compared with the spin-wave spectra of MnV$_2$O$_4$ [4,28], the symmetric lowest-energy spin wave should be the $\Gamma_1$ originates from strong fluctuations of $V^{3+}$ spins on the $B$ site in the CFI phase prior to their true canting below $T_{N2}$. Such spin fluctuations of $V^{3+}$ affect the Fe spin waves and therefore lead to the anomalous spin-wave broadening in $T_{N2} < T < T_{N1}$.

Note that the spin-wave shapes at 90 and 3.5 K are very similar with only a shift of $\approx 0.5$ meV indicating that Fe$^{2+}$ spins are not influenced obviously below $T_{N2}$. This suggests that there is no significant spin frustration at the Fe$^{2+}$ site in the NCFI/ferroelectric phase, consistent with powder neutron diffraction results that show the direction of the Fe$^{2+}$ spins remains along the $c$ axis below/above $T_{N2}$. Therefore, the Fe spins without magnetic frustration at the $A$ site are not mainly responsible for the appearance of the ferroelectricity below $T_{N2}$. Instead, the competition between the AFM $J_{V,V}$ and AFM $J_{Fe,Fe}$ induces strong spin frustration at the $V$ site resulting in the canting of $V^{3+}$ spins, which plays a major role in the appearance of the ferroelectricity based on (extended) spin-current models [7,14,29].

As shown in Fig. 4(b), the spin waves in FeV$_2$O$_4$ exhibit a significant broadening but without softening at the zone boundary, $\Gamma \approx 0.7$ meV for $H \leq 2.2$, but shows a significant increase/step to $\approx 3$ meV above $H \approx 2.4$. In Fig. 4(c), the average $\Gamma/E$ ratio $\approx 0.11$ is much smaller than that of the metallic ferromagnetic La$_2$-Sr$_1+\gamma$Mn$_2$O$_7$ with $\Gamma/E \approx 0.33-0.46$ [30], consistent with the high insulating behavior of FeV$_2$O$_4$ [7]. Furthermore, the $\Gamma/E \approx 0.07$ at the zone center and $\approx 0.14$ at the zone boundary exhibit weak $q$ sensitivity of $\Gamma/E$ and $\Gamma$ is not linear with respect to $E$. All these features exclude magnon-electron scattering [30] as the main mechanism for spin-wave broadening. Theoretical calculations [31] have shown that magnon-phonon coupling can increase the spin-wave damping without softening the dispersion. Dai et al. [32] reported a significant spin-wave broadening at the zone boundary with a step in $\Gamma$ in a few manganese perovskites and demonstrated the role of magnon-phonon coupling as a mechanism of such anomalous broadening. The existence of a strong coupling between spin, orbital, and lattice degrees of freedom [7] and the step in $\Gamma$ in FeV$_2$O$_4$ imply that magnon-phonon coupling plays the main role in the spin-wave broadening without softening at the zone boundary.

IV. CONCLUSION

In summary, neutron-scattering studies on FeV$_2$O$_4$ crystal reveal the different roles of two orbital-active Fe$^{2+}$ at the $A$ site...
and \(V^{3+}\) at the \(B\) site in the magnetic excitations. The strong spin-orbit coupling at the \(Fe^{2+}\) \(A\) site induces a significant energy gap below \(T_{N1}\) with little contribution from the \(V^{3+}\). The absence of a change in energy gap below \(T_{N2}\) is evidence for a very weak SO coupling or significantly quenched orbital moment of the \(V^{3+}\). The important role of orbital-active \(Fe^{2+}\) at the \(A\) site on the magnetic excitations is expected to be applicable to other spinels with orbital-active ions at that site, such as \(ACr_2O_4\) (\(A = Fe^{2+}\) or \(Cu^{2+}\)).

Comparing the Fe spin waves below and above \(T_{N2}\) precludes significant spin frustration at the \(Fe^{2+}\) site, indicating \(Fe^{2+}\) may not play an important role in inducing ferroelectricity and the ferroelectricity mainly results from the canting of \(V\) spins with strong frustration at the \(B\) site. The anomalous spin-wave broadening is observed in the collinear ferrimagnetic phase indicative of possible \(V^{3+}\) spin fluctuations prior to their true canting in the noncollinear ferrimagnetic phase. The spin-wave broadening also exists at the zone boundary without obvious spin-wave softening due to magnon-phonon coupling.

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