Multiferroicity and spiral magnetism in FeVO$_4$ with quenched Fe orbital moments

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(Rceived 27 October 2009; published 7 December 2009)

FeVO$_4$ has been studied by heat capacity, magnetic susceptibility, electric polarization and single-crystal neutron-diffraction experiments. The triclinic crystal structure is made of $S$-shaped clusters of six Fe$^{3+}$ ions, linked by VO$_4^{3-}$ groups. Two long-range magnetic ordering transitions occur at $T_{N1}=22$ K and $T_{N2}=15$ K. Both magnetic structures are incommensurate and below $T_{N2}$, FeVO$_4$ becomes weakly ferroelectric coincidentally with the loss of the collinearity of the magnetic structure in a very similar fashion than in the classical TbMnO$_3$ multiferroic material. However we argue that the symmetry considerations and the mechanisms invoked to explain these properties in TbMnO$_3$ do not straightforwardly apply to FeVO$_4$. First, the magnetic structures, even the collinear structure, are all acentric so that ferroelectricity in FeVO$_4$ is not correlated with the fact magnetic ordering is breaking inversion symmetry. Regarding the mechanism, FeVO$_4$ has quenched orbital moments that questions the exact role of the spin-orbit interactions.

DOI: 10.1103/PhysRevB.80.220402

There has been a recent surge of interest in a certain class of magnetoelectric materials,1 the type-II multiferroics, where ferroelectricity arises below a magnetic phase transition as a direct consequence of complex magnetic ordering.2 The phenomenon results from lowering of the magnetocrystalline symmetry to a polar group, and it is indeed found in compounds fulfilling strict magnetostructural symmetry requirements.3,4 It typically appears in systems subjected to magnetic frustration or strong exchange competition, as in Ni$_3$V$_2$O$_8$ (Ref. 3) or TbMnO$_3$.3,5

Besides symmetry considerations, type-II multiferroics must possess a microscopic mechanism to generate electric-dipole moments. A variety of such mechanisms have been proposed:6 magnetostriction is the only allowed mechanism for acinet collinear structures, and is active in the Ising system Ca$_3$(Co$_{0.5}$Mn$_{0.5}$)$_2$O$_6$ (Ref. 7) and, most likely, in the commensurate phase of YMn$_2$O$_5$.5 Most other “type-II” multiferroics are cycloidal magnets, where noncollinear spins are key ingredients in the context of the so-called spin-current model.6,7 For this, a crucial role is played by relativistic spin-orbit interaction, which can take place at the ligand ionic site, as for pure $e_g$ systems, within the transition-metal $t_{2g}$ orbitals or between $t_{2g}$ and $e_g$ orbitals.6 A particularly interesting case of the latter is provided by high-spin $d^5$ systems ($S=5/2$) where $L=0$ in the free ion and the orbital angular momentum is supposedly absent. As for the acinet and noncollinear magnetic structure itself, antisymmetric spin exchange brought by spin-orbit interactions becomes important in materials having a connected network of strong symmetric exchange interactions such as superexchange (SE) interactions, which can be destabilized by the presence of either strong next-nearest-neighbor interactions or by geometrical frustration.1,11

In this Rapid Communication, we describe a multiferroic compound—FeVO$_4$—in which the magnetic ion is orbitally quenched Fe$^{3+}$ ($d^5$, $L=0$, $S=5/2$). The magnetic and dielectric phase diagram of FeVO$_4$, as determined from magnetization, specific-heat and neutron-diffraction measurements, is that of a typical cycloidal magnet: ferroelectricity appears below $T_{N2}=15$ K, coinciding with the appearance of a noncollinear incommensurate magnetic structure (phase II), whereas a second collinear incommensurate magnetic phase (I), stable between $T_{N1}=22$ K and $T_{N2}$, is not ferroelectric. Uniquely, FeVO$_4$ does not contain connected magnetic direct-exchange or SE paths, and the magnetic modulation is primarily determined by a network of super-super-exchange (SSE) interactions. These pathways form loops connecting an odd number of Fe$^{3+}$, suggesting that frustration plays a key role in promoting noncollinearity and ferroelectricity.

Polycrystalline samples and single crystals were prepared following the procedures described in Refs. 12 and 13. Electric measurements and specific-heat and magnetic-susceptibility measurements were carried out on dense pellets of polycrystalline FeVO$_4$ using a physical properties measurement system Quantum design cryostat. The electrical polarization was derived from integration of the pyroelectric polarization measurements on single crystals were made with a vertical-field superconducting quantum interference device magnetometer using a horizontal axis sample rotator. Single-crystal neutron nuclear and magnetic Bragg-peak intensities were collected and at $T=2$ K and $T=18$ K on the four-circle diffractometer D15 ($\lambda=1.174$ Å) at the Institut Laue-Langevin (ILL), France. All the nuclear and magnetic structure refinements were carried out with the program FULLPROF.14

The crystal structure of FeVO$_4$ is shown in Fig. 1. To facilitate the description of the magnetic structures (see below) we have redefined the triclinic basis vector $c$ so that $c=-2a'\mathbf{+}c'$, where $a'$ and $c'$ are the basis vectors used in Ref. 13. The important crystallographic features for the description of the magnetic properties are easily identified. The Fe$^{3+}$ ions, all in the high-spin state $S=5/2$ (see below), are arranged in clusters, separated by (VO$_4$)$_{3-}$ groups, containing nonmagnetic V$^{5+}$ ions. Each cluster of 6 Fe$^{3+}$ ions consists of two identical Fe$_3$O$_{12}$ monomers, related by a center of inver-
consistent with a frustration index of /H20849/H11011. The contribution, indicated by the dashed line in Fig. 2, of the specific heat was determined by subtracting the lattice Debye function from the data at high temperature to the Debye function estimated by fitting the data at high temperature to the Debye function of 3 T and recording magnetization data between 5 and 35 K. At low temperatures, the direction of minimal susceptibility coincides with the direction of growth of the needle-shaped crystals (approximately along the crystallographic direction a). With this field orientation, labeled H, in the specific heat was determined by subtracting the lattice Debye contribution from the data at high temperature to the Debye function estimated by fitting the data at high temperature to the Debye function.

To obtain further insight into the nature of the magnetic ordering taking place at T, the data show Bragg peaks of magnetic origin, which can all be indexed with a single, nearly temperature-independent propagation vector k = (0.222 − 0.089 0.012) almost perpendicular to c. In the most general case of a single-k incommensurately modulated structure, the magnetic moments Mj(Rj) on a given crystallographic site describe an ellipse as they propagate in different unit cells Rj. Mj(Rj) can therefore be written as

\[ M_j(R_j) = A_j \cos(2\pi \cdot k \cdot R_j + \phi_j) + B_j \sin(2\pi \cdot k \cdot R_j + \phi_j) \]

where A and B are two perpendicular vectors defining the major and minor semiaxes of the ellipse. An initial set of
FIG. 3. (Color) Zoom in on the magnetic order of the Fe S-shaped cluster of Fig. 4 containing the surrounded spin. The three inequivalent Fe sites are shown as small red, green, and blue spheres, and the Fe sites with primed labels are obtained by inversion symmetry. The Fe are arranged in two types of edge-sharing polyhedra: two Fe\textsuperscript{3+}O\textsubscript{4} trigonal bipyramids (sites 2-2′) and the four other sites in Fe\textsuperscript{3+}O\textsubscript{6} octahedra. Spin are aligned with a common direction \( A \) at \( T=18 \) K, and rotate in the same (\( A, B \)) plane at \( T=2 \) K. The magnetic-moment amplitudes (black labels) were calculated using Eq. (1) with the refined parameters given in the supplementary information (Ref. 17), accounting for a dephasing term of 68.4° coming from the position of the cluster in the crystal [\( \mathbf{R}_{ij} = (0 \ 2 \ 1) \)]. Only the values of the refined phases \( \varphi_i \) are given in degrees (red labels) for clarity.

refinements indicated that the magnetic structure of phase I is a collinear spin-density wave (i.e., \( B_j=0 \)), whereas phase II possesses a helical structure. It is noteworthy that the collinear direction of the spins in phase I coincides with the major semiaxis \( A_j \) of the ellipses in phase II, indicating that the spin anisotropy does not change at the phase boundary. In principle, both the amplitudes and directions of \( A_j \) and \( B_j \) as well as the phase angles of the modulations can be different for each site. We have shown that the correlation between parameters can be significantly reduced by introducing constraints\(^{17} \) while still yielding refinements of excellent quality. This has lead us to consider only minimal models for phase I (10 parameters, \( R_{p2}=10.3\% \) and \( \chi^2=1.7 \)) and phase II (14 parameters, \( R_{p2}=5.07\% \) and \( \chi^2=8.2 \)). The constraints retained suggest that the data do not support significantly different orientations of the ellipses and that the amplitudes \( |A_j| \) and \( |B_j| \) (Fig. 3) of atoms related by centrosymmetry do not differ significantly, although their phases are not related by centrosymmetry and need to be determined independently. Perspective views of the magnetic structures of phases I and II are shown for one cluster in Fig. 3 and for few clusters in Fig. 4.

At \( T=2 \) K, the helical magnetic order reveals different degree of frustration in different directions. It is characterized by the presence of quasi-1D AF order on chains of S-shaped clusters running in the \( e \) direction. The SSE path linking clusters in this direction is therefore probably the least frustrated SSE interaction inducing only very slow rotations of the average AF direction over a very long period of approximately 110 nm. This contrasts with all the other SSE paths, which induce large rotations of the average AF direction between neighboring chains.

Noteworthy is that all the magnetic orders, including the collinear phase I, are acentric. The anisotropic behavior naturally comes from the phase difference for each pair of sites related by inversion symmetry, which all significantly deviate from 180° (Fig. 3). This inversion symmetry breaking is obvious at \( T=2 \) K, and the phases are such that each half cluster of 3 Fe shows an almost perfect AF order, but between the two halves, the AF directions are canted by 15 – 20°. As similar phases are refined at \( T=2 \) K and \( T=18 \) K, the collinear magnetic order at \( T=18 \) K essentially appears as the projection of the helical order on the common \( A \) direction, which is why it is also acentric. This situation is different than in prototype cycloidal magnets Ni\textsubscript{3}V\textsubscript{2}O\textsubscript{8} or TbMnO\textsubscript{3}, where the magnetic symmetry breaking of the inversion symmetry is claimed to be a crucial ingredient for the emergence of ferroelectric behavior and was only ascribed to the spiral phase.\(^{3,4} \) Here, ferroelectricity essentially results from a transition to a noncollinear magnetic order in the ground state below \( T_{N2} \).

The onset of a collinear order at higher temperatures has already been discussed by Mostovoy.\(^{10} \) In the high-temperature regime above \( T_{N2} \), anisotropy dominates so that the moments align along the local easy axis, whereas below, the reduction in entropy enables ordered components of moment in directions orthogonal to it. For FeVO\textsubscript{4} the local easy axis is the \( A \) direction deduced from the neutron data, which coincides with the macroscopic easy axis determined from the magnetization measurements and labeled \( H_{II} \) in Fig. 2(b). In phase II the moments are confined to the plane of the ellipses with \( A \) and \( B \) as semiaxes, drawn in Figs. 3 and 4. When a field is applied in any direction orthogonal to \( A \) (\( H_{II} \)) the temperature dependence of the magnetization shows a singularity at \( T_{N2} \), a rapid fall below \( T_{N2} \) and almost no singularity at \( T_{N1} \). The orthogonal direction for which the fall is most pronounced is parallel to \( B \), the minor axis of the ellipse. The noncollinearity of phase II reflects the appearance of a second-order parameter modulating moments oriented parallel to \( B \) stabilized by the presence of additional terms in the free energy which outweigh the entropy effect. The non-collinearity suggests that these terms are due to antisymmet-
ric spin-orbit coupling of the Dzyaloshinski-Morya-type proportional to vector products of spins $S_i \times S_j$. Most theories of multiferroic spiral magnets have invoked this interaction as the driving force leading to magnetically induced ferroelectricity, even if it is yet unclear if it arises from spin currents\(^9\) or the emergence of ion displacements.\(^9\)

In summary, we have demonstrated magnetically induced ferroelectricity in FeVO\(_4\). It is noteworthy that its magnetoelectric phase diagram in the vicinity of $T_{N1}$ is very similar to that of the classical TbMnO\(_3\) system in the vicinity of $T_{N2}$ = 27 K.\(^5\),\(^20\) However, there are important differences distinguishing FeVO\(_4\) from known type-II multiferroic materials, which challenge the theories describing the mechanism of multiferroic behavior and the symmetry of the multiferroic state. Inverse Dzyaloshinski-Morya interactions may not be here the sole active mechanism, since the Fe\(^{3+}\) ions have $L = 0$ in the free-ion state and because in FeVO\(_4\) the breaking of inversion symmetry of the magnetic order occurs in both phase I and phase II, so it is not correlated with the ferroelectric properties, which appear in phase II only. Besides, FeVO\(_4\) highlights better the connection between the exchange frustration and the magnetic order. In TbMnO\(_3\) or Ni\(_3\)V\(_2\)O\(_8\) such connection is harder to identify because the SSE interactions form a network of next-nearest-neighbor interactions interpenetrating that of the first neighbor superexchange interactions. In FeVO\(_4\) we have established a clear connection between the moment reductions or the spin rotations, which are typical of the incommensurate magnetic phases of spiral magnets, and the most relevant exchange paths giving rise to the magnetic frustration.

We thank J. A. Rodriguez-Velazman for his assistance during the neutron-diffraction experiment at the ILL.

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\(^{15}\)This observation is consistent with a strong magnetic diffuse scattering signal above $T_{N1}$, in neutron powder-diffraction experiments, which we also performed separately in the $T_{N1} < T < 30$ K temperature range. A more detailed account of all these observations will be reported elsewhere.

\(^{16}\)The measurements in all configurations ($H_\perp$ and $H||$) are in fact both sensitive to $T_{N1}$ and $T_{N2}$. This is due to the fact the crystal was misaligned with the rotator axis, leading to $10^\circ$ errors in precision for all the given directions.

\(^{17}\)See EPAPS Document No. E-PRBMD-80-R06946 for the details of the refinement procedure, the parameters, and reliability factors of the neutron-diffraction study of the magnetic structures of FeVO\(_4\). For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.

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