Weak Ferromagnetism and Field-Induced Spin Reorientation in $K_2V_3O_8$

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(Received 22 June 2000; revised manuscript received 13 October 2000)

Magnetization and neutron diffraction studies of the 2D $S = 1/2$ antiferromagnet, $K_2V_3O_8$, indicate an ordered state exhibiting weak ferromagnetism and field-induced spin reorientations. Of particular interest is the behavior in a basal plane magnetic field where a unique spin reorientation is observed in which the spins rotate from the easy c axis to the basal plane while remaining normal to the applied field. The experimental observations are well described by a two spin exchange model incorporating Heisenberg and Dzyaloshinskii-Moriya interactions with an additional c-axis anisotropy.

DOI: 10.1103/PhysRevLett.86.159 PACS numbers: 75.25.+z, 75.30.Gw

The physics of low dimensional quantum antiferromagnets is among the forefront problems in condensed matter physics. In this letter, we report magnetization and neutron scattering studies of a $S = 1/2$ 2D square lattice antiferromagnet, $K_2V_3O_8$, which reveal a startling and unexpected spin reorientation effect. Specifically, we find that a magnetic field applied in the plane of the square lattice causes a continuous rotation of the spins from a zero field orientation normal to the plane to an in-plane orientation normal to the field direction. This behavior is quite distinct from other, more conventional spin reorientations, such as spin-flop transitions, and suggests a novel competition between interactions in $K_2V_3O_8$.

Although $K_2V_3O_8$ is a quantum system, we show that the effect can be qualitatively understood in terms of a classical model Hamiltonian incorporating Heisenberg exchange, Dzyaloshinskii-Moriya (DM) interactions [1,2], and an easy axis anisotropy. Typically, only the antisymmetric term of the DM interaction is relevant, but the novel behavior in $K_2V_3O_8$ relies heavily on inclusion of the symmetric component of the DM interaction [3–7].

$K_2V_3O_8$ crystallizes in a tetragonal unit cell with space group $P4bm$ and lattice constants $a = 8.870$ Å and $c = 5.215$ Å [8]. The structure is shown in Fig. 1(a) and consists of magnetic V^{4+}-O_5 pyramids, nonmagnetic V^{5+}-O_4 tetrahedra, and interstitial K^+ ions. Previous magnetic measurements consisted of powder magnetization from 5–300 K [9] which were best described by a 2D Heisenberg model with coupling constant $J = 12.6$ K and a g value of 1.89. EPR measurements on single crystals suggest very small anisotropy with g values of $g_c = 1.922$ and $g_{ab} = 1.972$ [10]. Liu *et al.* [9] suggested from observation of field-dependent magnetization that $K_2V_3O_8$ may order at lower temperatures.

Single crystal plates of $K_2V_3O_8$ (typical dimensions: $1 \times 1 \times 0.1$ cm^3) were grown in a platinum crucible by cooling appropriate amounts of VO_2 in a molten KVO_3 flux. Additional details of the crystal growth will be reported elsewhere [11]. One of these single crystals was mounted in a quantum design SQUID magnetometer equipped with a sample rotator and the magnetization is shown in Fig. 2 as a function of both temperature (a) and applied magnetic field (b) for fields applied along both the c axis and within the tetragonal basal plane. The $M(T)$ data [Fig. 2(a)] were measured by cooling in the presence of a 100 Oe applied magnetic field while the $M(H)$ data [Fig. 2(b)] were taken by cooling to base temperature in zero field. From Fig. 2(a), the magnetization is seen to be very isotropic for temperatures in excess of about 8 K, confirming the Heisenberg nature of the interactions. At high temperatures, we observe a Curie-Weiss susceptibility with an effective moment $\{\mu = g\mu_B[S(S+1)]^{1/2}\}$ of $1.7\mu_B$ per formula unit (f.u.). This result is consistent with the presence of two nonmagnetic V ions per f.u. and one magnetic ion with $S = 1/2$.

The temperature dependence in the presence of a weak magnetic field shows a clear ordering phase transition below a temperature of about 4 K. The rapid decrease of the magnetization below this temperature with field applied along the c axis is indicative of antiferromagnetic ordering

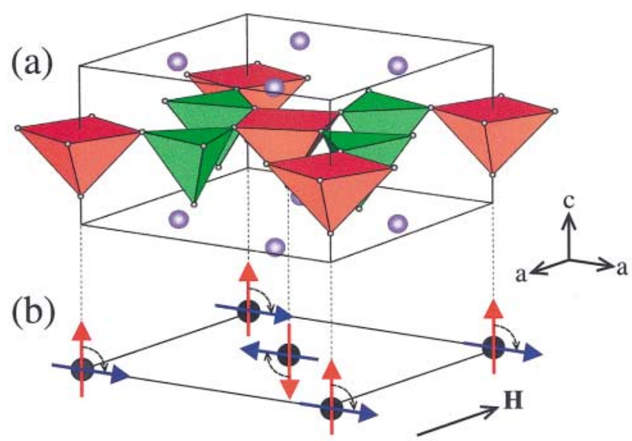

FIG. 1 (color). (a) The crystal structure of $K_2V_3O_8$ composed of magnetic V^{4+}-O_5 pyramids and nonmagnetic V^{5+}-O_4 tetrahedra. (b) The projection of the V^{4+} positions showing the location of the magnetic moments. The red arrows represent the zero field spin configuration and the blue arrows denote the behavior of the system in the presence of a basal plane magnetic field (in the direction shown by **H**).

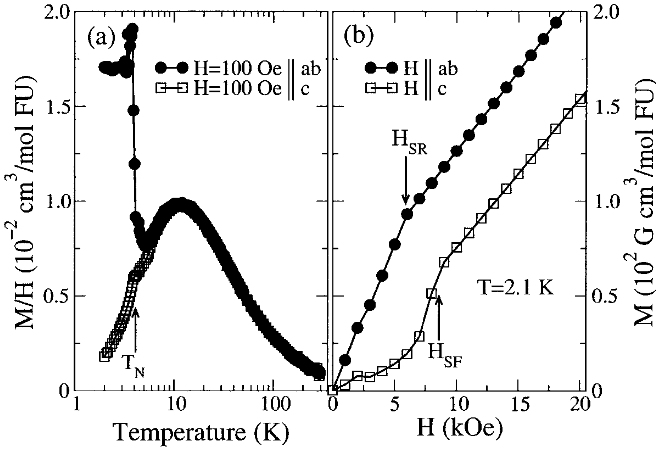

FIG. 2. (a) The temperature dependence of the dc susceptibility in a small applied magnetic field. For temperatures in excess of about 8 K, the system is seen to be very isotropic. Below 4 K, the system undergoes a phase transition to an antiferromagnetic state characterized by an *easy* c axis and weak ferromagnetic behavior in the basal plane. (b) The magnetization as a function of applied magnetic field for temperatures well below the ordering temperature. Field-induced phase transitions are observed for field applied in the basal plane (H_{SR}) and along the c axis (H_{SF}).

with an easy axis along c. However, measurements within the basal plane show a clear ferromagnetic enhancement upon entering the ordered state. The ferromagnetic ordered moment is small ($\sim 3 \times 10^{-4} \mu_B/V^{4+}$ in a 100 Oe applied field) and thus we conclude that the system is antiferromagnetic with spins primarily along the c axis and a small canted moment in the basal plane.

The behavior of the magnetization as a function of field for temperatures well below the Néel temperature is shown in Fig. 2(b). For field applied along c, we observe an abrupt increase in magnetization above 8.5 kOe, consistent with a discontinuous spin-flop phase transition, further confirming the easy nature of the c axis. For fields within the basal plane, we observe an intriguing field-induced phase transition which occurs at a magnetic field of $H_{SR} = 6.5$ kOe. There was no evidence of irreversibility in $M(H)$ for either field orientation or in angular rotations of the sample in the presence of an applied field, and no evidence of thermal hysteresis was observed.

To investigate the detailed microscopic spin arrangement, neutron diffraction measurements were performed on the HB1A and HB1 triple-axis spectrometers at the High Flux Isotope Reactor in Oak Ridge National Laboratory. For the measurements in zero field, the sample was mounted in the $(h0l)$ scattering plane and comparison of scattering at 1.6 and 10 K indicated the presence of magnetic Bragg peaks [in the $(h0l)$ plane] described by integer indices with h odd. These peaks suggest a magnetic unit cell in which the corner and face-center moments within the basal plane are aligned antiparallel with parallel alignment along the c axis. Examination of the integrated intensities of six magnetic reflections indicated that the moments lie along the c axis consistent with conclusions drawn from the magnetization measurements. The value of the ordered moment per ion ($\mu = g\mu_B S$) was found to be $0.72(4)\mu_B$ at $T = 1.6$ K, reduced from the expected value of $1\mu_B$. This can likely be attributed to quantum fluctuations in the low-dimensional $S = 1/2$ system. The zero field magnetic structure is shown schematically by the red arrows in Fig. 1(b).

To examine the behavior in the presence of a basal plane magnetic field, the crystal was mounted in the $(h0l)$ scattering plane and a vertical field applied along the (010) direction. The field dependence of the (100) and (101) magnetic Bragg peaks are shown in Figs. 3(a) and 3(b). As the intensity of magnetic neutron scattering is proportional to the component of magnetic moment normal to the wave vector transfer, Q, the observed disappearance of the (100) magnetic Bragg peak and the concomitant enhancement of the (101) reflection are consistent with a continuous rotation of the spins from the (001) to the (100) direction with increasing magnetic field strength. The rotation is complete at a field strength of $H_{SR} = 6.5$ kOe, in excellent agreement with the anomaly in the magnetization. This is shown schematically by the blue arrows in Fig. 1(b). Thus, we conclude that this transition is a peculiar spin-

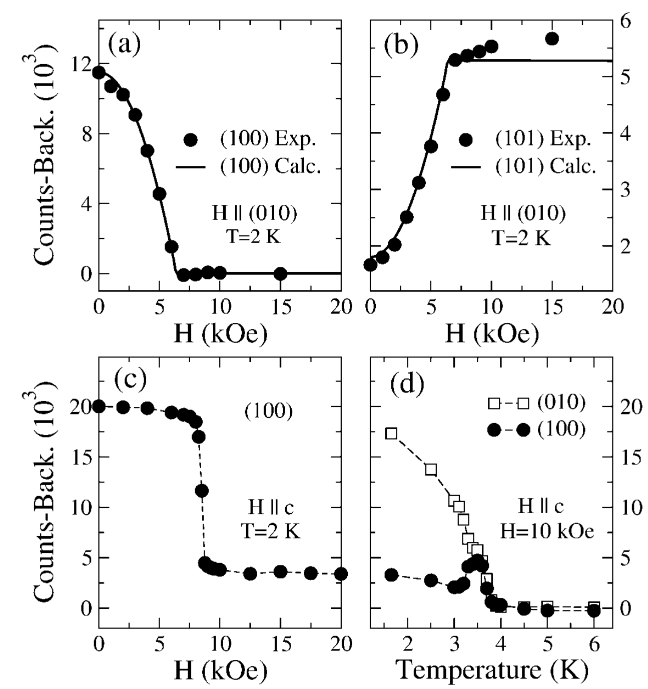

FIG. 3. The background subtracted intensity of diffracted neutrons as a function of applied magnetic field [along the (010) direction], for temperature well below the Néel temperature, is shown for the (100) and (101) magnetic Bragg peaks in panels (a) and (b). The solid lines represent calculations based on the model described in the text. (c) The field dependence of the (100) Bragg reflection with field applied along the c axis, for temperature well below the ordering temperature, showing a discontinuous spin-flop phase transition. (d) The temperature dependence of (100) and (010) in an applied field of 10 kOe.

reorientation phase transition whereby the spins rotate from the c axis to the basal plane while remaining normal to the applied field direction.

A second crystal was mounted in the ($hk0$) scattering plane to allow measurements with field applied along the c axis. The results of these measurements are shown in Figs. 3(c) and 3(d). As a function of applied magnetic field, the (100) Bragg peak intensity drops abruptly upon passing through a field of 8.5 kOe, suggesting a discontinuous reorientation of the spins. The temperature dependence in an applied field of 10 kOe shows a strikingly different behavior for the (100) and (010) Bragg peaks, and the weaker intensity for (100) suggests that the moments have "flopped" from the c axis into the basal plane selecting a specific direction within the basal plane in close proximity to the (100) direction. No evidence for a structural distortion has been observed and the selection of a specific direction likely results from a slight misalignment of the magnetic field with the c axis. This misalignment was less than 1° for the measurements performed but even this level may induce a net field in the basal plane of sufficient strength to overcome domain energies thus selecting a specific magnetic domain. Such a domain selection has been observed in the tetragonal antiferromagnet MnF_2 [12].

Weak ferromagnets often have at their origin the competition between the antisymmetric DM interaction and the symmetric Heisenberg interaction [13]. To consider the DM interactions in $K_2V_3O_8$, we consider the projection of the crystal structure onto the tetragonal basal plane, as shown in Fig. 4(a). The plane of inversion symmetry between near-neighbor V^{4+} spins, represented by the dashed lines in Fig. 4(a), results in DM vectors located in that inversion plane [13] giving components along (110) and (001) directions, denoted by $\mathbf{D}_{xy}$ and $\mathbf{D}_z$, respectively (these directional vectors are indicted in the figure relative to the central site). The fourfold rotation symmetry through the central site gives rise to the configuration of $\mathbf{D}$ vectors shown in the figure. From the neutron diffraction measurements, we know that the magnetic unit cell contains two spins in both zero and nonzero fields and, hence, we will consider a two-spin Hamiltonian. Noting that, in summing over the near-neighbor spins, the components of the DM vectors in the basal plane (i.e., the $\mathbf{D}_{xy}$ terms) cancel, we write the two-spin, mean-field Hamiltonian as

$$\mathcal{H}_{12} = 8J\mathbf{S}_1 \cdot \mathbf{S}_2 + 8D_z(\mathbf{S}_1 \times \mathbf{S}_2)_z \,, \qquad (1)$$

where $(\mathbf{S}_1 \times \mathbf{S}_2)_z$ is the z component of the vector cross product and the factor of 8 comes from the four near neighbors and two sublattices.

The Hamiltonian [Eq. (1)] has a ground state spin configuration with spins in the basal plane and, consequently, an additional c-axis anisotropy is required to account for the easy c axis observed experimentally. Thus, we add a c-axis anisotropy of the form $E_z S_{1z} S_{2z}$ and, with addition

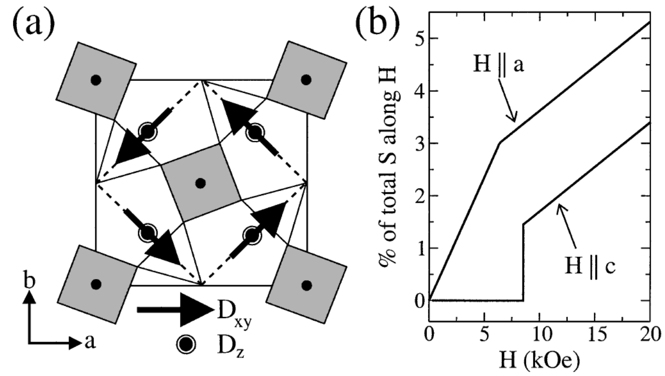

FIG. 4. (a) The projection of the crystal structure onto the tetragonal basal plane. The magnetic moments are located at the center of the shaded squares, and the triangles represent the V^{5+}-O_5 tetrahedra. The components of the Dzyaloshinskii-Moriya vectors (D_{xy} and D_z) are shown in the figure relative to the central spin. (b) The calculated component of magnetic moment along the field direction as a function of applied field for field applied along both a and c. This result compares very well to the $M(H)$ data plotted in Fig. 2(b).

of the Zeeman energy for nonzero field, we arrive at the Hamiltonian,

$$\mathcal{H}_{12} = 8J\mathbf{S}_1 \cdot \mathbf{S}_2 + 8D_z(\mathbf{S}_1 \times \mathbf{S}_2)_z + 8E_z S_{1z} S_{2z} - g\mu_B \mathbf{H} \cdot (\mathbf{S}_1 + \mathbf{S}_2) \,. \qquad (2)$$

With the assumption of classical spins, this rather simple, mean-field, Hamiltonian describes all of the low temperature properties of the system. For appropriate values of D_z and E_z, the spins point along the c axis, in zero applied field, with canting observed in small basal plane magnetic fields due to the normal competition between DM and Heisenberg interactions. For fields applied in the basal plane, the Zeeman energy and DM interaction favor arrangement of the spins in the basal plane. This competes with the c-axis anisotropy, causing a continuous rotation of the spins to the basal plane with increasing field strength. The spins remain primarily normal to the applied field direction to minimize the Zeeman energy. Finally, with field applied along the c axis, a spin-flop transition occurs due to competition between Zeeman energy and the c-axis anisotropy, causing an abrupt rotation of the spins into the basal plane.

As we have two field-induced phase transitions, we can estimate the values for D_z/J and E_z/J required to produce phase transitions at the measured field values (using $J = 12.6$ K [9], $g_c = 1.922$ [10], and the ordered moment $\mu = g\mu_B\langle S\rangle = 0.72\mu_B$). This results in a value of $D_z/J = 0.04$ and $E_z/J = 1.2 \times 10^{-3}$. This value of D_z/J is in excellent agreement with the measured g values [9,10] ($D_z/J \sim \Delta g_c/g_c$ [13], where Δg_c is the deviation of g_c from the spin only value of 2: $g_c = 1.922$ [10] gives $D_z/J \sim 0.041$). By using these values, we can calculate the induced magnetic moment along the field direction for field applied along both the a and c axes, and the results are plotted in Fig. 4(d) as a function of applied magnetic field in kOe. These results can be directly compared to the $M(H)$ data plotted in Fig. 2(b) and the qualitative agreement is remarkable, suggesting that this relatively simple model adequately describes the low temperature properties of the system. To further emphasize this, we have superimposed on Figs. 3(a) and 3(b) the calculated magnetic Bragg peak intensity for the (100) and (101) reflections in the presence of an applied magnetic field along the (010) direction. These results are represented by the solid lines in Figs. 3(a) and 3(b) and the agreement between the calculations and the data is excellent, particularly for the (100) reflection. The agreement for the (101) reflection is very good for field strengths up to H_{SR} but deviates slightly for higher fields. The reason for this disagreement could be a field-dependent $\langle S \rangle$ which may result from field-dependent suppression of quantum fluctuations, as has been observed in some ABX_3 antiferromagnets [14].

To shed some light on the nature of the c-axis anisotropy, we calculate the symmetric component of the DM interaction. The addition of this term causes a rescaling of J to $(J\text{-}D^2/4J)$ and the inclusion of a symmetric anisotropy term $(1/2J)\mathbf{S}_1 \cdot \mathbf{A} \cdot \mathbf{S}_2$, where $\mathbf{A}$ is a 3×3 matrix with elements $A_{uv} = D_u D_v$ [5,15]. Making these changes and summing over near-neighbor spins produces the Hamiltonian,

$$\mathcal{H}_{12} = 8\left(J - \frac{D_z^2}{4J}\right)\mathbf{S}_1 \cdot \mathbf{S}_2 + 8D_z(\mathbf{S}_1 \times \mathbf{S}_2)_z + 8\left(\frac{D_z^2}{2J} - \frac{D_{xy}^2}{4J}\right)S_{1z}S_{2z} - g\mu_B \mathbf{H} \cdot (\mathbf{S}_1 + \mathbf{S}_2). \tag{3}$$

This Hamiltonian has precisely the same form as Eq. (2) and, consequently, the c-axis anisotropy falls out naturally upon inclusion of both the symmetric and antisymmetric DM interactions. The estimated value for the c-axis anisotropy (normalized to J) in Eq. (3) is 7.5×10^{-4} (using $D_z/J = 0.04$ and estimating D_{xy}/J from the measured $g_{ab} = 1.972$). Within the level of approximation involved in this model, this is in reasonably good agreement with the observed value of 1.2×10^{-3}. Consequently, we conclude that $K_2V_3O_8$ represents a unique system where the *qualitative* features rely on the inclusion of the symmetric anisotropy term. The only known clear evidence of this symmetric anisotropy occurs in the DM spiral system $Ba_2CuGe_2O_7$, where the addition of this term is necessary to produce *quantitative* agreement between experiment and theory [7]. As a caveat, it is important to note that we cannot rule out other possible mechanisms for this additional anisotropy. Rather, we simply note that inclusion of this symmetric anisotropy alone, which is necessary to properly consider DM interactions, seems to adequately describe the properties of the system. Finally, we note that quantum fluctuations have not been included in the above model and, consequently, further theoretical work is needed to completely describe the properties of this $S = 1/2$ system.

In summary, we have observed a phase transition in $K_2V_3O_8$ with an antiferromagnetic ordered state accompanied by weak ferromagnetism. We observe a conventional spin-flop phase transition with field applied along the c axis and a unique spin reorientation in the presence of a basal plane magnetic field. Remarkably, this rich magnetic behavior can be well described by a simple, classical, mean-field model incorporating Heisenberg exchange together with DM interactions and an additional c-axis anisotropy. This additional anisotropy can, at least partially, be accounted for by inclusion of the symmetric component of the DM interaction, suggesting that $K_2V_3O_8$ is a unique system where introduction of this interaction is necessary to describe the *qualitative* behavior of the system.

We acknowledge stimulating discussions with G. Murthy, M. W. Meisel, R. Coldea, and D. A. Tennant. Oak Ridge National Laboratory is managed by UT-Battelle, LLC, for the U.S. Department of Energy under Contract No. DE-AC05-00OR22725.

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