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## letters to nature

field lines are puzzling, however. In principle, the plasma should fall freely along such lines, reaching speeds of 50 km s<sup>-1</sup> or more, but that conflicts with the speeds in fact seen (a few kilometres per second). A somewhat similar situation prevails in spicules, also without a satisfactory explanation.

Why has counter-streaming not been detected in previous Doppler observations of filaments? We made Dopplergrams from pairs of red-wing and blue-wing images, as have many other authors<sup>4-14</sup>. We concluded that our line-of-sight velocity maps alone do not reveal counter-streaming because a simple subtraction of moderateresolution images, taken in opposite wings, will usually result in a null Doppler signal. Second, motions of the chromospheric background can corrupt the signal in the filament, unless spatial resolution is sufficiently high. Last, isolated pairs of images do not reveal the long distances traversed by the moving knots of mass.

Detection of the counter-streaming requires high spatial resolution, a favourable filament orientation, time-series of observations in both wings simultaneously over several hours, carefully registered images and a high rate of image projection. The filament we observed is quite typical. We therefore suggest that counter-streaming is a feature common to all quiescent filaments.

Our observations contradict all contemporary prominence models, even those of barbs, as these models do not allow any

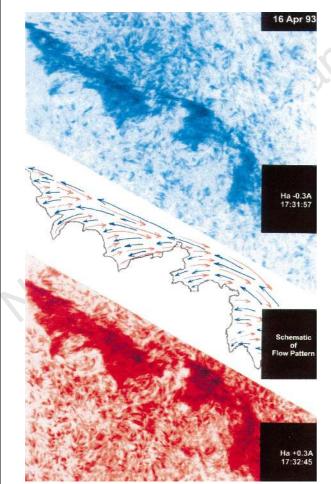


Figure 2 Images on 16 April, showing the inclined threads. In the blue wing, the streaming is only westward along the spine and downward into the barbs on the near side of the filament (blue arrows in the middle panel). In the red wing, the streaming is only eastward along the spine and up in the same barbs on the near side (red arrows in middle panel). This systematic pattern appears most clearly on 16 April, when the filament lay just inside the east limb. Finally, on April 20, when the filament had crossed the central meridian, the pattern reverses, with a predominant eastward streaming in the blue wing although both eastward and westward streaming are seen in different filament threads.

vertical motions, let alone counter-streaming. Simply allowing horizontal field lines to drift up and down, while carrying blobs of mass, will not easily explain counter-streaming, for then alternate field lines would have to pass each other and travel long diagonal distances. Such complex motions seem unrealistic to us.

We propose instead a conceptual model<sup>18</sup> in which field lines bend down from the spine to the chromosphere (see Fig. 2 centre). In this model, the mass flows along the field lines: it is not carried by moving horizontal field lines, and does not cross the field lines. The tension of such steeply inclined field lines, which are embedded in the prominence sheet, might act to restrain the prominence from erupting. Certainly the existence of such field lines needs to be incorporated in any acceptable model of prominence eruption.  $\square$ 

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# **Temperature-induced** magnetization reversal in a YVO<sub>3</sub> single crystal

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The total energy of a magnet in a magnetic field is lowest when the magnetic moment is aligned parallel to the magnetic field. Once aligned, the magnetic moment can be reversed by applying a sufficiently large field in the opposite direction. These properties form the basis of most magnetic recording and storage devices. But the phenomenon of magnetization reversal in response to a change in temperature (in a small magnetic field) is rarer. This effect occurs in some ferrimagnetic materials consisting of two or

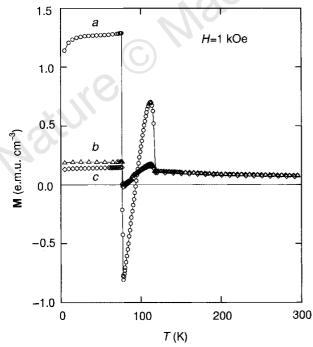
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more types of antiferromagnetically ordered magnetic ions<sup>1</sup>, and forms the operational basis of ferrimagnetic insulators. Here we report the observation of multiple temperature-induced magnetization reversals in YVO<sub>3</sub>. The net magnetic moment is caused by a tilting of the antiferromagnetically aligned moments of (crystallographically identical) V<sup>3+</sup> ions, due to orthorhombic distortion in the crystal structure. We observe an abrupt switching at 77 K associated with a first-order structural phase transition, and a gradual reversal at  $\sim\!95~\text{K}$  without an accompanying structural change. The magnetization always reverses if the crystal is cooled or warmed through these two temperatures in modest fields. We propose a possible mechanism involving a change in orbital ordering which may be generic to a broad class of transition metal oxides.

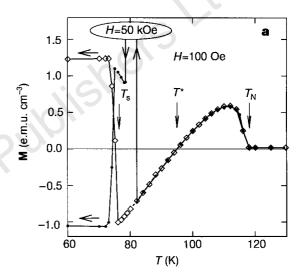
Transition metal oxides with the perovskite structure display a large variety of properties such as high-temperature superconductivity, colossal magnetoresistance<sup>2,3</sup> and very diverse magnetic properties. We now report on another novel and peculiar phenomenon in YVO<sub>3</sub>: multiple and reversible sign changes in the magnetization with temperature. Such magnetic-moment reversals have been observed in those ferrimagnets<sup>1</sup> with strong magnetic anisotropy that exhibit a compensation temperature. The net magnetization, initially oriented parallel to the field, changes sign at this temperature and the metastable, energetically unfavourable state is fixed by the strong anisotropy. For such an effect to occur, inequivalent sites must exist. In YVO<sub>3</sub>, however, all magnetic V sites are equivalent, as shown by the crystallographic data.

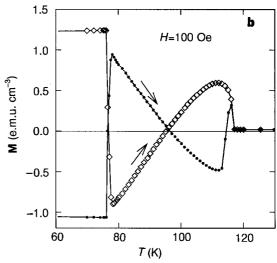
Close to our situation is the observation of a 'diamagnetic' response in LaVO<sub>3</sub> (refs 4–6). Upon weak-field cooling, this system exhibits a magnetization opposite to the applied magnetic field below a structural phase transition temperature  $T_{\rm t}=138~{\rm K}< T_{\rm N}=142~{\rm K},$  where  $T_{\rm N}$  is the magnetic ordering (Néel) temperature. It has been suggested that this diamagnetic



**Figure 1** Temperature dependence of the magnetization in an applied magnetic field of 1 kOe along the a-, b- and c-axes, respectively. Upon cooling the sample in a fixed magnetic field H < 4 kOe below  $T_{\rm N} = 116$  K, the magnetization after first increasing starts decreasing and crosses zero at  $T^* \approx 95$  K to a large negative value. With further cooling, it jumps at  $T_{\rm s} = 77$  K to a large positive value. This second transition exhibits hysteresis that is consistent with a first-order transition, as inferred from the structural data. In contrast with LaVO $_3$ , we observe not only an abrupt magnetization reversal at the first-order transition  $T_{\rm t}$ , but also a gradual reversal near 95 K.

response is due to a reversal of a canted-spin moment on traversing the first-order Jahn–Teller phase transition at  $T_{\rm t}$  below which the orbital angular momentum is maximized<sup>6–8</sup>, and that the response of the orbital moment to the forces generated at the first-order phase transition can reverse the Dzyaloshinsky vector so as to create a canted spin in a direction opposite to the applied field, given that  $T_{\rm t}$  is close to  $T_{\rm N}$ . Other polycrystalline samples of V<sup>3+</sup> perovskites show weak indications of anomalous behaviour<sup>7–9</sup>. We demonstrate the dramatic behaviour of single crystals of YVO<sub>3</sub> in which multiple magnetization switching is clearly observed. In contrast with LaVO<sub>3</sub>, YVO<sub>3</sub> provides a wide temperature window between  $T_{\rm N}$  and the first-order phase transition which we refer to as  $T_{\rm s}$ , enabling us to study the effect in detail. Furthermore, an additional magnetization reversal is observed, irrespective of the cooling conditions.





**Figure 2** Magnetization versus temperature in a field of 100 Oe, demonstrating the memory effect upon the application of large fields. In the curve marked by filled circles in **a** we follow **M** with decreasing temperature down to a temperature below  $T^*$ ; a high field is then applied to flip the magnetization positive, after which the field is lowered again to 100 Oe and the temperature decreases. The curve marked by diamonds is measured without intermediate application of the high field. In **b**, we show the curves with increasing temperature starting from below  $T_s$ : the curve marked by diamonds without having 'trained' the sample, and the curve marked by filled circles after 'training' as described for **a**. This demonstrates the reversibility: upon warming, **M** now switches from negative below  $T_s$ , to positive for  $T_s < T < T^*$ , and becomes negative for  $T > T^*$ . It is thus nearly a 'mirror image' of the behaviour shown in Fig. 1 and the diamond marked curve in **b**, except that it becomes positive again close to  $T_N$ .

YVO<sub>3</sub> has a distorted perovskite structure of the type GdFeO<sub>3</sub> (crystal symmetry *Pbnm*) at all temperatures. It has two magnetic phases: one at  $T_{\rm s} \approx 77~{\rm K} < T < T_{\rm N} = 116~{\rm K}$  and another at  $T < T_{\rm s}$ . The detailed magnetic structure of these phases is controversial<sup>10,11</sup> but is not crucial for the experimental observations reported here.

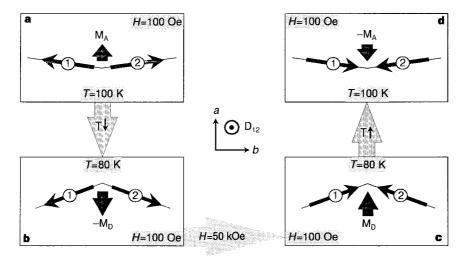
The distorted crystal structure naturally leads to canted spin structures. As the oxygen ions mediating the superexchange interaction between the two nearest neighbour V ions are not at an inversion centre, the antisymmetric Dzyaloshinsky-Moriya (DM) interaction of the form  $\mathbf{D} \cdot (\mathbf{S}_1 \times \mathbf{S}_2)$  will be present, where **D** is the so-called Dzyaloshinsky vector and  $S_1$  ( $S_2$ ) are the V spins corresponding to the two magnetic sublattices. The DM interaction, which prefers canted spin arrangements, is in competition with the quite different ordinary Heisenberg exchange  $JS_1 \cdot S_2$ , which prefers collinear spin arrangements. Also, because the oxygen octahedra coordinating the V ions are twisted to form a staggered V-O bond direction along the c-axis, the single-ion anisotropy easy axis is staggered. Both of these mechanisms can lead to weak ferromagnetism<sup>12</sup>. The fact that YVO<sub>3</sub> is a weak ferromagnet with spin canting has been established from measurements on powder samples<sup>13</sup>. Several batches of crystallographically pure large single crystals ( $5 \times 5 \times 5 \text{ mm}^3$ ) were grown by the floating-zone method. The magnetic measurements made on a large number of our single crystals all reveal the same unusual behaviour, with several magnetization reversals upon cooling in a weak magnetic field (Fig. 1).

Even more striking, is the observation of a memory effect shown in Fig. 2a. This indicates that the sign of the magnetization can be reversed by the application of a large enough field, but that upon lowering the field, the temperature-dependent net magnetic moment  $\mathbf{M}(T)$  always changes sign, irrespective of what its sign was, when crossing  $T_s$  both on cooling and warming. The same is also true for the second crossing at T.

Although we do not as yet have a detailed microscopic theory for the magnetization reversal with temperature, we propose the model shown in Fig. 3. As mentioned above, there are two mechanisms for producing a canted spin structure in these materials: single-ion magnetic anisotropy and DM coupling. These two canting mechanisms produce the net moment in the a-c plane, and in our model we assume that they are oriented in opposite directions. We checked that the observed phenomena are connected to spin canting: the differential susceptibility  $d\mathbf{M}/dH$  is always positive (even in the 'diamagnetic' state) and the net moment is  $\sim$ 0.01 Bohr magneton per V ion, which for an S=1 system corresponds to a canting angle of  $\sim$ 0.2°.

Using this model, we present in Fig. 3 a pictorial view of what could happen as a function of temperature. We start at temperatures just below  $T_{\rm N}$  (Fig. 3a). Here, the two sublattice spins prefer to lie close to a local easy axis if the local magnetic anisotropy is large, resulting in a net magnetic moment, as shown. As T decreases, this net moment will first grow because of the development of a sublattice magnetization due to superexchange. However, as the sublattice magnetization develops, so does the DM coupling, which tends to cant the spins in the opposite direction. Consequently, the net moment will reach a maximum and then decrease. It crosses zero at the temperature below which the DM interaction dominates. This will result in a moment opposite to the small applied field. It could only reverse to its lowest energy state in the field by reversing the two sublattices on a macroscopic scale, resulting in a frozen in metastable state (Fig. 3b). A large external magnetic field can overcome the barrier for rotation of the sublattice spins, resulting in a reversal of the sublattice spin orientation (Fig. 3c). The net moment is now oriented parallel to the field and will remain so upon lowering the field. If we now increase the temperature, we return to the situation where magnetic anisotropy dominates. Thus, the net moment will change sign again, now turning negative for T > 95 K (the curve marked by filled circles in Figs 2b, 3d). Once we get close enough to  $T_N$ , the energy barrier for the reversal of the sublattice magnetization will eventually become very small. Any finite field will flip the net moment again to a positive value and reach a maximum just below  $T_N$ , dropping to zero at  $T_N$  (Fig. 2). This model explains all the data from high temperatures down to the first-order phase transition at 77 K.

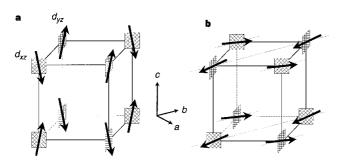
The magnetization reversal at  $T_s$  remains more of a puzzle. It follows from our results that the ferromagnetic moment is oriented along the a-axis both above and below  $T_s$ . From neutron scattering, we know that the magnetic structure changes at  $T_s$  from C- to G-type, as proposed by Kawano  $et\ al.^{11}$  This is definitely connected with a change of orbital ordering occurring at  $T_s$ . Low-temperature single-crystal X-ray diffraction (Y.R.  $et\ al.$ , unpublished results) of YVO<sub>3</sub> shows that, whereas above  $T_s$  the V–O bond lengths are almost equal, the first-order phase transition is accompanied by a strong distortion of these bond lengths, resulting in pairs of long (2.052 Å), intermediate (1.992 Å) and short (1.975 Å) V–O bonds. The long and short bonds are oriented alternately along the [110] and [110] in the basal a-b plane, whereas the intermediate one of 1.992 Å is along the c-axis, similar to the structure of LaMnO<sub>3</sub>; such a distortion corresponds to orbital ordering, with the  $d_{xy}$ 



**Figure 3** Pictorial view of the temperature dependence of the magnetization. **a**, Just below  $T_{\rm N}$ , the two sublattice spins prefer to lie close to a local easy axis if the local magnetic anisotropy is large, resulting in a net magnetic moment parallel to the applied field. **b**, As T decreases below  $T^* = 95\,\rm K$ , the DM interaction dominates which tends to cant the spins in opposite direction. A large external magnetic field

can overcome the barrier for rotation of the sublattice spins, resulting in a reversal of the sublattice spin orientation.  $\mathbf{c}$ , The net moment is now oriented parallel to the field and will remain so upon lowering the field. If we now increase the temperature, we come back to the situation where the magnetic anisotropy dominates.  $\mathbf{d}$ , Thus, the net moment will change sign again, turning negative for T > 95 K.

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**Figure 4** Suggested orbital ordering below and above  $T_s = 77 \, \text{K}$ . **a**, A C-type orbital ordering with a G-type spin ordering; and **b**, a G-type orbital ordering with a C-type spin ordering. The dotted lines are along the b-axis. The hatched squares indicate the planes in which the occupied d orbitals lie. The  $d_{xy}$  orbitals that are in each case occupied by one electron are omitted for clarity.

orbital occupied at each V<sup>3+</sup> site and the second electron occupying, respectively, the  $d_{xz}$  and  $d_{yz}$  orbitals in two sublattices as shown in Fig. 4. According to the Goodenough–Kanamori rules<sup>14</sup>, this orbital occupation naturally leads to the G-type antiferromagnetism<sup>11</sup>. A similar result was also obtained by band-structure calculation<sup>15</sup>. From Fig. 1, we see that the ferromagnetic component is both above and below  $T_s$  oriented parallel to the a-axis of the crystal; the magnetic structure above  $T_s$  must therefore be of C-type. Then, according to Bertaut's symmetry considerations<sup>12</sup>, the easy axis below  $T_s$  should be close to the c direction in order for the weak moment to remain along a. From this, we conclude that the easy axis must indeed change on going through the phase transition. The Ctype magnetic ordering observed between  $T_s$  and  $T_N$  (ref. 11) should then correspond to an orbital structure, with the alternation of the sublattices also being along the c direction and, as discussed above, with the easy axis almost parallel to b. Such a drastic change of the magnetic properties at  $T_s$  can lead to a change in the relative role of the DM interaction and the anisotropy. Careful neutron scattering experiments are needed to clarify the behaviour of YVO<sub>3</sub> across  $T_s$ .

Our results make it difficult to compare LaVO<sub>3</sub> and YVO<sub>3</sub> in detail: single crystals of LaVO<sub>3</sub> are needed, although the close proximity of  $T_N$  and  $T_t$  in LaVO<sub>3</sub> will be a complicating factor.  $\square$ 

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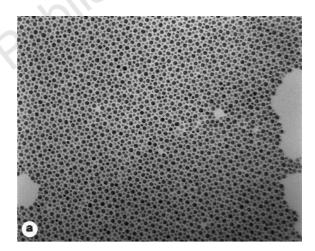
# Spontaneous ordering of bimodal ensembles of nanoscopic gold clusters

C. J. Kiely\*, J. Fink\*†, M. Brust†, D. Bethell† & D. J. Schiffrin†

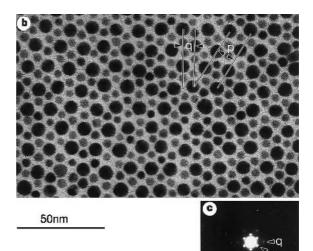
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The controlled fabrication of very small structures at scales beyond the current limits of lithographic techniques is a technological goal of great practical and fundamental interest. Important progress has been made over the past few years in the preparation of ordered ensembles of metal and semiconductor nanocrystals<sup>1-7</sup>. For example, monodisperse fractions of thiol-stabilized gold nanoparticles<sup>8</sup> have been crystallized into two- and three-dimensional superlattices<sup>5</sup>. Metal particles stabilized by



100nm



**Figure 1** An ordered raft comprising Au nanoparticles of two distinct sizes with  $R_{\rm B}/R_{\rm A}\approx 0.58$ . Shown are electron micrographs at low (**a**) and higher (**b**) magnification. **c**, The low-angle superlattice electron diffraction pattern obtained from this bimodal raft structure.