

## Heat capacity and magnetic properties of a $\text{EuVO}_3$ single crystal

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We have studied the heat capacity and magnetic properties of a  $\text{EuVO}_3$  single crystal. The compound undergoes an orbital ordering transition at  $T_{\text{OO}}=204$  K, which is then followed by a spin ordering transition at  $T_{\text{SO}}=131$  K. In the spin ordered region, we have found that the compound is very sensitive to small trapped fields present in the superconducting solenoid of a magnetometer during cooling. Large negative Weiss temperatures are seen along all principal crystallographic axes indicating that strong antiferromagnetic interactions are present in this compound. Nevertheless, at low temperatures, we observed open hysteresis loops with a relatively high remanent magnetization and coercivity. We discuss the results for  $\text{EuVO}_3$  in terms of an inhomogeneity with random fields.

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Recently, much attention has been paid to the  $R\text{VO}_3$  compounds ( $R$ =rare earth or Y), in which the intrinsic frustration between spin and orbital degrees of freedoms is believed to be crucial to the understanding of the interplay between the different ordering mechanisms.<sup>1-3</sup> As a result, these compounds exhibit unusual magnetic properties such as a temperature induced magnetization reversal,<sup>4</sup> staircaselike and glassylike behaviors,<sup>5</sup> and magnetic memory effects.<sup>6</sup> Early powder neutron diffraction studies for the  $R\text{VO}_3$  compounds<sup>7</sup> (except for  $R$ =Sm, Gd, and Eu, which strongly absorb neutrons) have indicated that there are two possible magnetic structures. For the compounds with a larger rare earth radius (from La to Dy), the magnetic structure is of a  $C$  type; i.e., the spins order antiferromagnetically in the  $ab$  plane and ferromagnetically along the  $c$  axis. On the other hand, compounds with smaller rare earth ionic radii (from Ho to Lu) have a  $G$ -type magnetic structure; i.e., the spins order antiferromagnetically along all three directions. According to the Goodenough-Kanamori rules,<sup>8</sup> the  $C$ - and  $G$ -type spin configurations should correspond to a  $G$ - and  $C$ -type orbital ordering (OO), respectively. Recently, single crystal neutron diffraction studies on  $\text{YVO}_3$  have indicated a change in the magnetic structure in the ordered region from the  $C$  type at high temperature to the  $G$  type at lower temperature.<sup>2</sup> Based on heat capacity and magnetization measurements, such a change in the magnetic structure in the ordered region was also suggested for some other compounds with the heavier rare earths ( $R$ =Dy to Lu).<sup>9</sup> However, results of recent powder neutron diffraction studies on  $\text{YbVO}_3$  (Ref. 10) and  $\text{LuVO}_3$  (Ref. 11) seem to rule out this possibility.

As mentioned previously, in the case of  $\text{EuVO}_3$ , neutron diffraction studies have yet to be carried out because of the strongly neutron absorbing nature of Eu. However, since Eu lies between La and Dy in the periodic table, it is reasonable to assume that it has the  $C$ -type antiferromagnetic (AF) structure. In earlier studies carried out on polycrystalline samples, Kimishima *et al.*<sup>12</sup> have observed that the magnetization of  $\text{EuVO}_3$  starts to increase at temperatures below 123 K until the lowest measured temperature of 77 K. This was claimed to be a result of the formation of a canted AF structure.<sup>12</sup> However, given the fact that most of the ortho-

vanadate compounds are very strongly antiferromagnetically coupled, a small amount of inhomogeneity, which has spins with weak random local fields, could also give rise to the ferromagneticlike behavior.<sup>4</sup> We have recently proposed such a scenario to account for some of the intriguing magnetic properties of the orthovanadates, including staircaselike hysteresis loops, a spin-glass-like behavior,<sup>5</sup> and a temperature induced magnetization reversal.<sup>4</sup> In this paper, we report on a study of the heat capacity and magnetic properties of single crystal samples of  $\text{EuVO}_3$ . Our analysis in this case again suggests that the observed ferromagneticlike behavior of the compound can also be qualitatively explained using a model of inhomogeneity with random fields.

Single crystal  $\text{EuVO}_3$  was grown by means of the floating zone technique using a high temperature xenon arc furnace. At first,  $\text{EuVO}_4$  was prepared by mixing the nominal composition of  $\text{Eu}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$  (with a purity of 99.9%), followed by annealing at 1100 °C for 48 h. The product was then reduced at 1000 °C in flowing  $\text{H}_2$  for 10 h to produce the  $\text{EuVO}_3$  powder phase. The  $\text{EuVO}_3$  feed and seed rods used for the single crystal growth were made by pressing the powder under hydrostatic pressure and then annealing these rods at 1500 °C under a flow of Ar.

Measurements of the *zero-field-cooled* (ZFC)<sup>13</sup> and field-cooled (FC) magnetization and the magnetic isotherms were carried out in a Quantum Design superconducting quantum interference device (SQUID) magnetometer. For the FC measurements, the sample was cooled from the paramagnetic region to 2 K in an applied field, and the data were then collected on warming. For the ZFC measurements, the sample was cooled in *zero* field to 2 K before a magnetic field was applied. The data were then taken on warming. Heat capacity measurements of the sample were carried out in a Quantum Design physical property measurement system with a heat capacity option using a relaxation technique.

In Fig. 1, we present the heat capacity of the  $\text{EuVO}_3$  compound as a function of temperature. Two lambda-shape anomalies are obvious, which are associated with the OO at  $T_{\text{OO}}=204$  K and the AF spin ordering (SO) transition at  $T_{\text{SO}}=131$  K. Our value of  $T_{\text{SO}}$  is higher than 123 K previously reported for a polycrystalline sample.<sup>12</sup> In Fig. 1, we

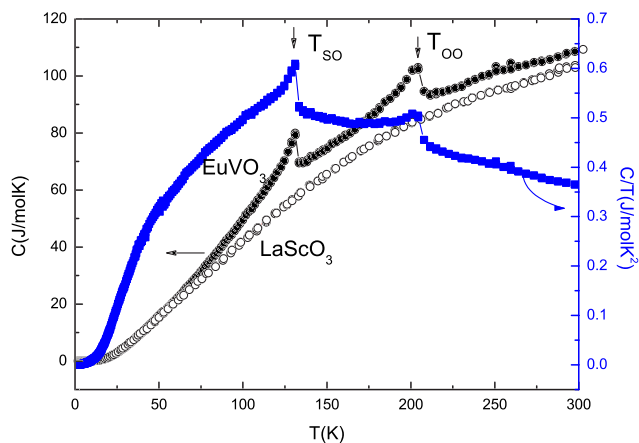


FIG. 1. (Color online) Heat capacity as a function of temperature for a  $\text{EuVO}_3$  single crystal and a  $\text{LaScO}_3$  polycrystalline sample.

also include the data of the heat capacity measured on a polycrystalline sample of the isostructural nonmagnetic compound  $\text{LaScO}_3$ . Because of the different molar masses of components between  $\text{LaScO}_3$  and  $\text{EuVO}_3$ , we scaled the temperature values in  $\text{LaScO}_3$  by a corresponding effective Debye temperature defined as (see, e.g., Ref. 14)

$$\Theta_{\text{eff}} = \frac{\Theta_D(\text{EuVO}_3)}{\Theta_D(\text{LaScO}_3)} = \left[ \frac{(M_{\text{Eu}})^{3/2} + (M_{\text{V}})^{3/2} + 3(M_{\text{O}})^{3/2}}{(M_{\text{La}})^{3/2} + (M_{\text{Sc}})^{3/2} + 3(M_{\text{O}})^{3/2}} \right]^{1/3}.$$

The phonon part of the heat capacity can then be subtracted from the data for  $\text{EuVO}_3$  to obtain the magnetic contribution to the heat capacity  $C_{\text{mag}}$ . The temperature dependence of  $C_{\text{mag}}$  and its corresponding magnetic entropy  $S_{\text{mag}}$  are displayed in Fig. 2. It can be seen from this figure that the  $S_{\text{mag}}(T)$  curve changes its slope at the OO and SO transitions. At the SO transition, the value of  $S_{\text{mag}}$  is about 7.8 J/mol K, which is close to  $R \ln 3 = 9.13$  J/mol K ( $R$  is the molar gas constant) expected for the vanadium ions with the three

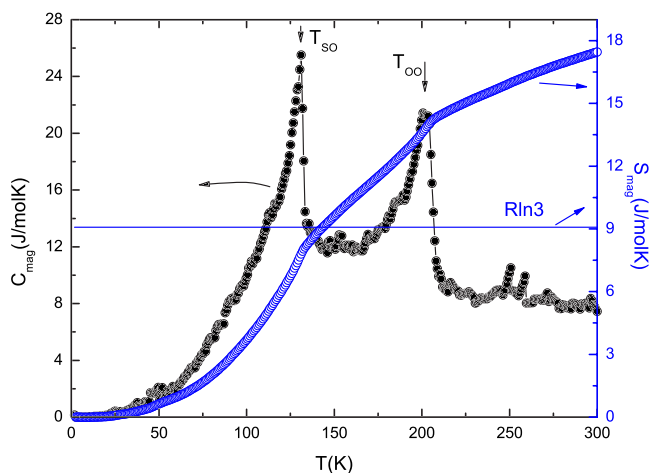


FIG. 2. (Color online) Temperature dependence of the magnetic contribution to the specific heat  $C_{\text{mag}}$  (left axis) and the magnetic entropy  $S_{\text{mag}}$  (right axis).

available orbital states  $d_{xy}$ ,  $d_{yz}$ , and  $d_{zx}$ . Above  $T_{\text{SO}}$ , the entropy keeps rising, reaching a value of 17.46 J/mol K at room temperature. Since the system is paramagnetic at  $T > T_{\text{SO}}$ , this “excess” entropy over  $R \ln 3$  cannot be magnetic in origin. Much of this entropy is associated with the structural phase transition accompanying the OO at  $T_{\text{OO}} = 204$  K. Above  $T_{\text{OO}}$ , there is clearly a positive but constant contribution to  $S_{\text{mag}}$  that is probably due to an imperfect subtraction of the phonon background since in this case there is a substantial molar mass difference between  $\text{EuVO}_3$  and  $\text{LaScO}_3$ . There may also be a contribution to  $S_{\text{mag}}$  from the Eu ions due to a mixing of thermally excited states into the  $J=0$  ground state of  $\text{Eu}^{3+}$  that gives rise to the Van Vleck paramagnetic contribution<sup>15</sup> to the magnetic susceptibility (see below).

The results of the *ZFC* and *FC* magnetization versus temperature runs are displayed in Fig. 3. From the figure, we can see that in a modest applied field (e.g.,  $H=0.1$  and 0.4 kOe), the results of the *ZFC* curve is affected by the small trapped field (TF) present in the superconducting magnet of the SQUID magnetometer. We have examined the TF carefully. Before each measurement, we ran a degauss sequence to minimize the TF; its absolute value is estimated to be less than 2 Oe. We can generate a TF with the opposite sign by reversing the sign of the magnetic fields in the degauss sequence.<sup>4</sup> In Fig. 3, it can be seen that the *ZFC* magnetization observed after cooling in a positive TF (*ZFC\_PTF*) is higher than that with negative TF (*ZFC\_NTF*) even though the TF is more than 2 orders of magnitude smaller than the applied field (e.g., of 0.4 kOe) used for the measurement. When the applied field is large enough (e.g.,  $H=1$  kOe), the effect of the small TF is suppressed entirely and the data for the *ZFC\_PTF* coincide with those of the *ZFC\_NTF*. It is well known that for conventional magnetic materials, the domain translation is reversible at (very) low magnetic fields,<sup>16</sup> and so the TF of the order of a few oersteds does not have any influence on the nominal *ZFC* results. However, this is clearly not the case for  $\text{EuVO}_3$ . It is very surprising that a TF of less than 2 Oe can create the irreversible magnetization at 1.8 K, which has a coercivity more than 2 orders of magnitude higher than the TF. We also note that the low field sensitivity seen here in  $\text{EuVO}_3$  appears to be a common feature among other  $R\text{VO}_3$  compounds including  $R=\text{La}$ ,  $\text{Nd}$ ,  $\text{Sm}$ ,  $\text{Y}$ ,<sup>4</sup>  $\text{Pr}$ ,<sup>5</sup> and  $\text{Gd}$ .<sup>6</sup> Another noteworthy feature of the magnetization versus temperature data for the  $\text{EuVO}_3$  compound is the splitting between the *ZFC* and *FC* curves and the form of the curves that are reminiscent of the response expected for a ferromagnetic material.

In order to explore further the magnetic properties of  $\text{EuVO}_3$ , in Fig. 4, we present the reciprocal of the magnetic susceptibility of the compound as a function of temperature in the paramagnetic region. All the curves follow a Curie-Weiss behavior, but with a change in the slope of the reciprocal of the magnetic susceptibility at the OO temperature  $T_{\text{OO}}$  of 204 K. A linear fit over the temperature intervals 150–200 and 210–300 K gives values for the Weiss temperature  $\theta_p$  and the effective moment  $\mu_{\text{eff}}$  listed in Table I. From these values, one can see that (i) in both temperature ranges, the observed Weiss temperatures  $\theta_p$  along all three principal axes are negative and large, which clearly indicates

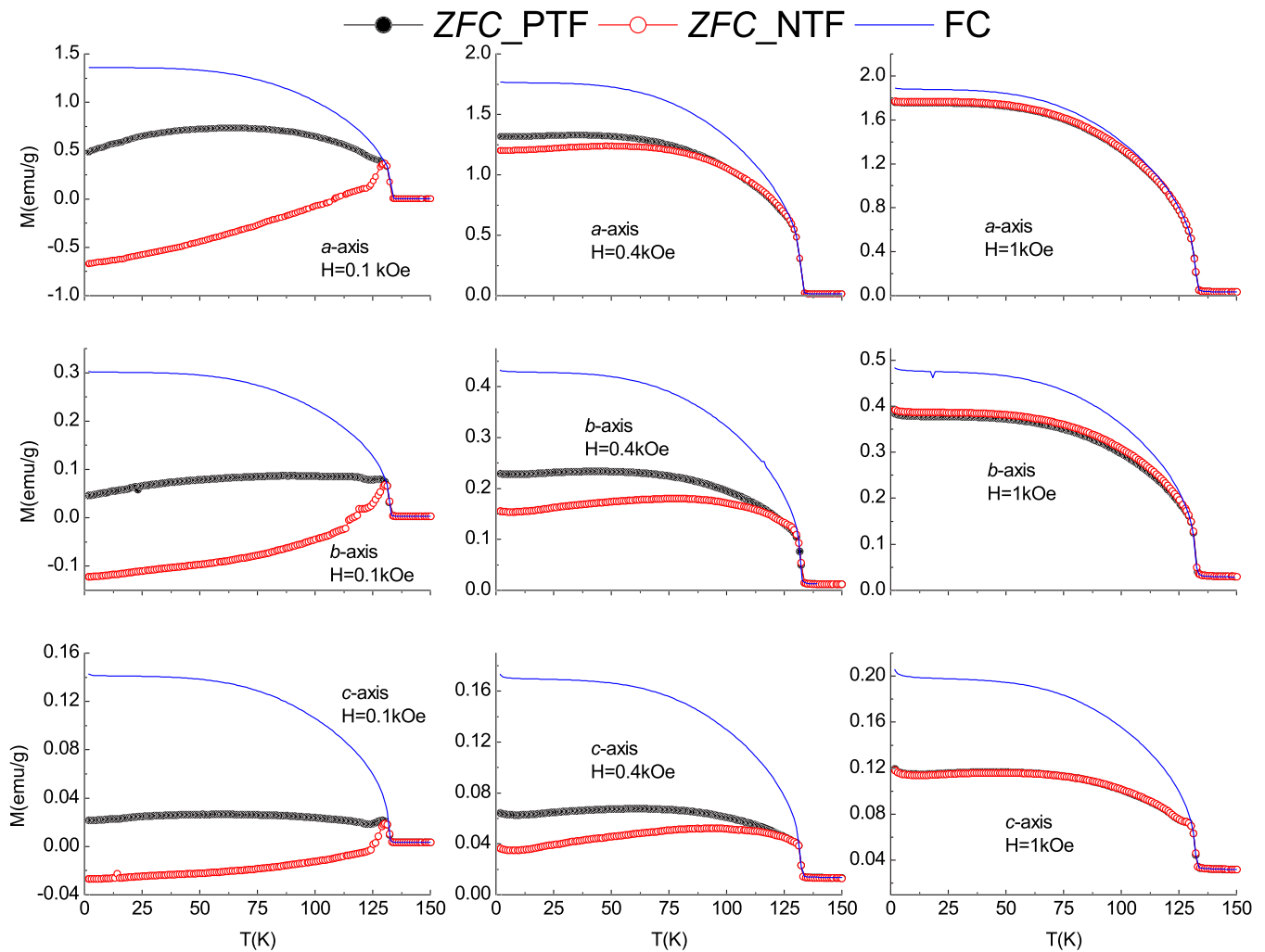


FIG. 3. (Color online) Zero-field-cooled ZFC and field-cooled (FC) magnetization versus temperature curves for a  $\text{EuVO}_3$  single crystal measured along the three main crystallographic axes at different applied fields. PTF and NTF refer to the positive and negative trapped field in the solenoid of the magnetometer, respectively.

the strong AF nature of the interactions present in the compound, and (ii) the observed effective moment  $\mu_{\text{eff}}$  ( $\text{EuVO}_3$ ) is much larger than the value of  $2.83\mu_B$  expected for the vanadium spin only with  $S=1$ . Although the lowest multiplet  $J$  given by Hund's rules for trivalent  $\text{Eu}^{3+}$  is zero, a mixing of the excited states into the  $J=0$  ground state results in a Van Vleck contribution to the paramagnetic susceptibility and a magnetic moment on the  $\text{Eu}^{3+}$ .<sup>15</sup> As a result, the system consists of two noninteracting spin systems in the paramagnetic region,  $\text{V}^{3+}$  and  $\text{Eu}^{3+}$ , and the effective moments can be estimated using the relationship  $\mu_{\text{eff}} = \sqrt{\mu_{\text{eff}}^2(\text{V}^{3+}) + \mu_{\text{eff}}^2(\text{Eu}^{3+})}$ .<sup>5</sup> Assuming  $\mu_{\text{eff}}(\text{V}^{3+}) = 2.83\mu_B$  (spin only,  $S=1$ ) and  $\mu_{\text{eff}}(\text{Eu}^{3+}) = 3.4\mu_B$ ,<sup>15</sup> an effective moment  $\mu_{\text{eff}}(\text{EuVO}_3) = 4.42\mu_B$  is obtained, which is close to the observed experimental value of  $5.16\text{--}5.91\mu_B$  listed in Table I. We note that in the fits we have used a simple Curie-Weiss law, without taking into account the presence of any crystal field effects. This could cause some fractional error in determining the “actual”  $\mu_{\text{eff}}$ . There may also be small contributions from other sources such as the off-stoichiometric composition.

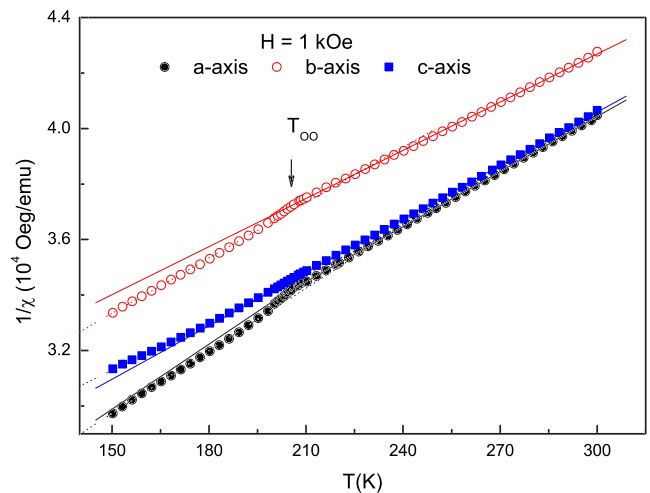


FIG. 4. (Color online) The reciprocal of the magnetic susceptibility as a function of temperature for a  $\text{EuVO}_3$  single crystal. The dotted lines represent the C-W fitting at low temperatures in 150–200 K, and solid lines at high temperatures in 210–300 K.

TABLE I. Values of the Weiss temperature  $\theta_p$  and effective moment  $\mu_{eff}$  as derived from a linear fitting of the inverse susceptibility versus temperature over different temperature ranges (150–200 and 210–300 K) in the paramagnetic state.

	<i>a</i> axis		<i>b</i> axis		<i>c</i> axis	
	$\theta_p$ (K)	$\mu_{eff}$ ( $\mu_B$ /f.u.)	$\theta_p$ (K)	$\mu_{eff}$ ( $\mu_B$ /f.u.)	$\theta_p$ (K)	$\mu_{eff}$ ( $\mu_B$ /f.u.)
150–200 K	–244.8	5.16	–350.5	5.49	–395.1	5.59
210–300 K	–310.95	5.5	–437.4	5.88	–333.1	5.91

The hysteresis loops for  $\text{EuVO}_3$  measured at 1.8 K with a magnetic field applied along each of the three principal crystallographic axes are presented in Fig. 5. The open hysteresis loops observed along all three axes are consistent with our previous observation of a splitting between the ZFC and FC magnetization data. The remanent magnetizations are  $M_r^a = 0.081\mu_B$ /f.u.,  $M_r^b = 0.021\mu_B$ /f.u., and  $M_r^c = 0.01\mu_B$ /f.u. along *a*, *b*, and *c* axes, respectively.

There are no features in either the magnetization or the heat capacity data that can be related to an ordering of the Eu moments. Our systematic studies of various  $R\text{VO}_3$  ( $R$ =rare earth) compounds have shown that, with the exception of  $\text{GdVO}_3$ , there appear to be no cases where an ordering of the rare earth moments can be inferred from the magnetic measurements.<sup>4–6</sup> Thus, below the SO temperature  $T_{SO}$  of 131 K, the magnetic ordering present in  $\text{EuVO}_3$  can be attributed solely to the vanadium magnetism. Here, our conclusion is in agreement with previous studies by Kimishima *et al.*<sup>12</sup>

The behavior of the ZFC and FC magnetization data and the open hysteresis loops indicate that  $\text{EuVO}_3$  is not a simple AF material. The high values for the negative Weiss temperatures  $\theta_p$  observed along all three principal axes, and the SO temperature indicate that very strong AF interactions are present in this material. Although crystal field effects result in different values of  $\theta_p$  being observed along different directions, these values should include the value of  $\theta_p$  for a system in which one need only consider the exchange

interactions.<sup>17</sup> This allows us to apply a simple *classical* model for a homogeneous antiferromagnet to the direction with the lowest absolute value of  $\theta_p$  to give an estimate of the AF interaction strength which is of the order of  $10^6$  kOe. On the other hand, there is a remanent magnetization observed along all three principal crystallographic axes. Since Eu is not magnetically ordered, the contribution to the remanent magnetizations is from the V sublattice only. Along the *a* axis, the remanent magnetization accounts for about 4% of the full  $V^{3+}$  moment of  $2\mu_B$  and about 1% and 0.5% along the *b* and *c* axes, respectively. We note that with the aforementioned estimated AF interaction strength of  $10^6$  kOe, to reach even 0.5% of the full  $V^{3+}$  moment of  $2\mu_B$  one would need an extremely high field of  $5 \times 10^3$  kOe.

In order to explain the relatively high magnetization values observed along all three main axes, one could argue that the system is a (homogenous) canted antiferromagnet and that the ferromagnetic component is quite easy to rotate in an applied field. This assumption, however, conflicts with the different values of the remanent magnetization observed along different axes and the fact that there is a (very) strong anisotropy between the magnetization along the *a* axis and that in the *bc* plane. Thus, arguments based on a homogenous canted AF do not seem to be able to account for the observed magnetic properties of  $\text{EuVO}_3$ .

Recently, we have proposed that the open hysteresis loops in the  $R\text{VO}_3$  compounds can be better understood in terms of an inhomogeneity associated with random field spins.<sup>4,5</sup> This

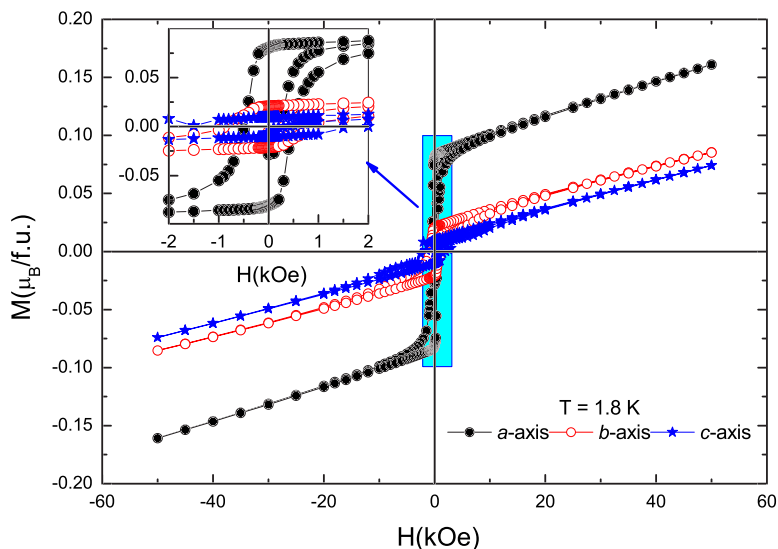


FIG. 5. (Color online) Magnetization versus applied field hysteresis loops measured along the main axes at 1.8 K of a  $\text{EuVO}_3$  single crystal.



model has been applied to diluted Ising antiferromagnets where there exists a small number of weak local field spins frozen like a spin glass, which are embedded in an infinite network of antiferromagnetically coupled spins (see, e.g., Refs. 4–6 and references therein). In the orthovanadate  $RVO_3$ , the one dimensional (Ising) orbital character has been well established.<sup>2,18–20</sup> We argue that defects in the orbital structure (or faulty orbitals), which have already been observed experimentally,<sup>21</sup> can act in a way that is similar to the dilution effect in the Ising antiferromagnets and that such defects lie at the origin of the random field spins.

In this scenario,  $EuVO_3$ , as well as some other  $RVO_3$  compounds, can be considered as consisting of weak local field spins (sublattice  $A$ ) embedded in the main matrix of strongly antiferromagnetically coupled spins (sublattice  $B$ ). We note that the weak local fields of the spins in sublattice  $A$  also imply that crystal field effects can lead to the reduced magnetic moment in the ordered state as well as to the anisotropy in the magnetization along different directions observed here in  $EuVO_3$ . In order to estimate the number of spins with weak local fields, we consider the ratio between  $M_r/M_s$ , where  $M_s$  is the saturation magnetization which is assumed to be  $2\mu_B$  corresponding to the full moment ex-

pected for  $V^{3+}$ . At 1.8 K, this ratio is largest along the  $a$  axis but still only requires 2% of the  $V^{3+}$  moments to be aligned parallel with the magnetic field. The remaining spins (sublattice  $B$ ), on the other hand, are strongly antiferromagnetically coupled, in accordance with the high negative Weiss temperatures observed along all three main axes, and thus they barely contribute to the observed magnetization signal at low temperature.

In summary, we have studied the magnetic properties of the  $EuVO_3$  single crystal. Even though high negative Weiss temperatures indicate that strong AF magnetic correlations are present in this compound, we have observed an unusual ferromagneticlike behavior in the *ZFC* and *FC* magnetization versus temperature curves and open hysteresis loops with relatively high remanent magnetizations along all three principal crystallographic axes. The unusual magnetic properties of this compound can be qualitatively accounted for by using our recently proposed model of inhomogeneity with random field.

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