Magnetic properties of LaVO$_3$

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Herein, we report on the magnetic properties of LaVO$_3$. We have observed diamagnetism in this compound, which is an antiferromagnetic insulator, below the Néel temperature under field-cooled conditions. We observe hysteresis in magnetization versus applied field $M(H)$ isotherms below the Néel temperature. LaVO$_3$ has a ferromagnetic component to the spin ordering, due to canting of spins and/or due to ferrimagnetism. Four-probe resistivity measurements rule out the possibility of superconductivity and the dimagnetism appears to be associated with uncompensated antiferromagnetism (ferrimagnetism). From our ^{51}V NMR measurements on LaVO$_3$ we associate the kink in susceptibility with magnetic ordering.

I. INTRODUCTION

The compound LaVO$_3$ has been reported to be a cubic perovskite[1] with $a_0 = 3.91$ Å, a cubic perovskite with $a_0 = 7.842$ Å,[2] a tetragonal distortion of the cubic perovskite,[3–7] and a hexagonal distortion of the cubic perovskite structure.[8] The compound undergoes a tetragonal $(c/\sqrt{2}a > 1)$ to orthorhombic $(c/\sqrt{2}a < 1)$ structural phase transition with decreasing temperature in the vicinity of 130 K.[6,9,10]

Four-probe electrical-resistivity measurements on a single crystal show activated conduction with an activation energy of 0.14 eV.[9]

The magnetic susceptibility exhibits a peak near 140 K, and a Curie-Weiss fit to the data above T_N yields a negative paramagnetic Curie temperature indicative of antiferromagnetic ordering.[4,6,7,9,11,12] The saturation moment at 4.2 K, as obtained from a neutron-diffraction investigation,[4,10] was found to be $1.3 \pm 0.1 \mu_B$, which is much less than the spin-only moment $(2\mu_B)$ expected for a $S = 1$ system such as V^{3+}, with $g = 2$. Dougier and Hagenmuller[6] found that LaVO$_3$ exhibited weak ferromagnetism below the Néel temperature.

Herein we present magnetic susceptibility and ^{51}V NMR data on LaVO$_3$. The susceptibility was found to be anomalous below the Néel temperature. We observed a large diamagnetism in magnetic fields up to a few kilogauss in the antiferromagnetic insulator LaVO$_3$. The ^{51}V NMR data confirm the appearance of magnetic order below the temperature at which the susceptibility shows an anomaly. We have observed a second signal which persists below the Néel temperature with a Knight shift which is independent of temperature.

II. EXPERIMENTAL DETAILS

LaVO$_3$ was prepared by arc-melting equimolar mixtures of predried La$_2$O$_3$ (99.99%) and V$_2$O$_3$ (95+ %) in an argon atmosphere on a water-cooled copper hearth. Another sample which made use of 99.9% pure V$_2$O$_3$ was also prepared by arc melting. The former is referred to as set 2 and the latter as set 3 in this paper (these samples

were part of a general study of the La$_x$Sr$_{1-x}$VO$_3$ system).

X-ray diffraction was performed on a Rigaku Geigerflex diffractometer ($\lambda = 1.5418$ Å). The observed peak positions were corrected for zero-point shift and nonlinearity using Si as an internal standard. The lattice parameters were obtained using a least-squares fitting procedure.

Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer, TGA 7, thermogravimetric analyzer. The vanadium oxidation state was determined from the weight gain on heating the sample to 1000 °C in oxygen and assuming that the final oxidation state of vanadium was +5.

dc resistivity measurements were performed with and without a magnetic field by the four-probe method. dc susceptibility was measured with a Quantum Design superconducting quantum interference device (SQUID) magnetometer.

^{51}V NMR measurements were performed both with a phase-coherent pulsed spectrometer in a field of 5.892 T and with a modified Varian continuous-wave (cw) spectrometer in a field of about 1 T. For the cw measurements, we used a Torgeson spectrometer,[13] Varian probe, and an electromagnet. The magnetic field was calibrated with an aqueous solution of AlCl$_3$.

III. RESULTS AND DISCUSSION

A. X-ray diffraction and TGA

Powder x-ray-diffraction analysis indicated the formation of a single-phase sample with a structure which was a tetragonal distortion of the cubic perovskite structure, $a = b = 5.556$ (± 0.002) Å and $c = 7.853$ (± 0.008) Å. The oxygen contents, as deduced from the TGA scans (see Fig. 1), were found to be 3.061 (set 2) and 3.020 (set 3), the precision of the measurement being ± 0.0001 and the accuracy ± 0.001.

B. Magnetic susceptibility and resistivity

The magnetic susceptibility of LaVO$_3$ (Fig. 2) exhibits a peak at ~140 K, indicative of antiferromagnetic order-
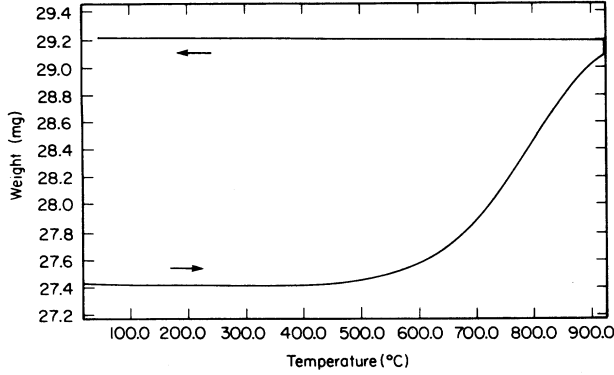

FIG. 1. TGA scan in pure oxygen for LaVO₃ (set 3).

The susceptibility below T_N depends on the cooling conditions (i.e., whether the sample is cooled in a field or not). In particular, note that the susceptibility is higher in the case of a zero-field cooled (ZFC) measurement as compared with that of a field-cooled (FC) measurement. Also, the compound LaVO₃ exhibits hysteresis in
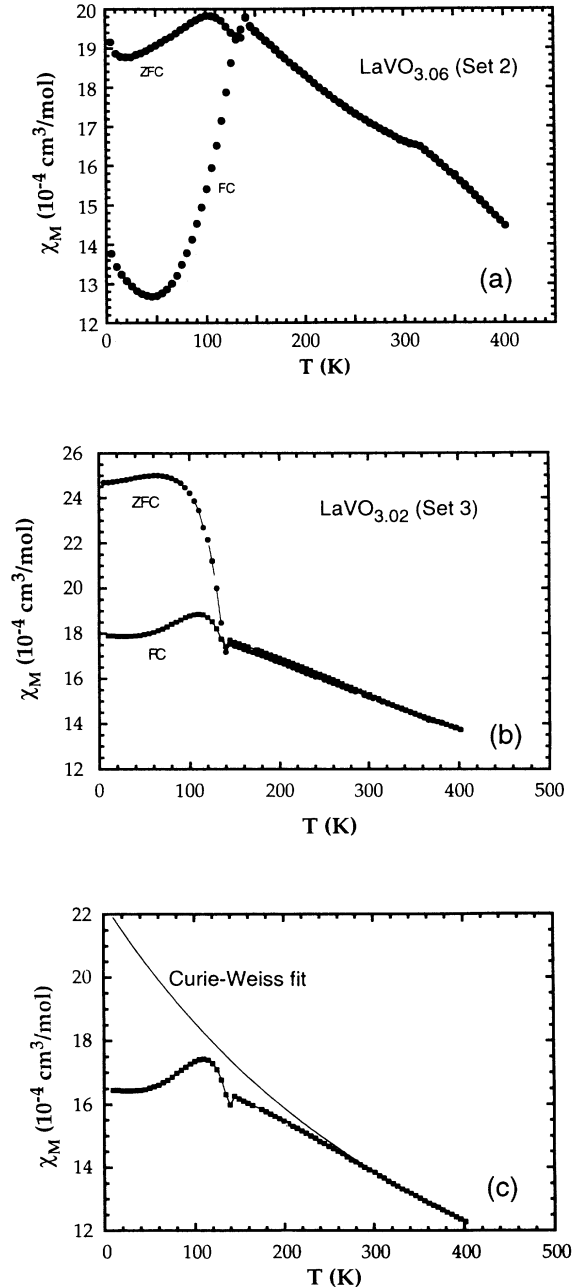
ing. The data below T_N are seen to be significantly different for the two samples. This may be related to the differing oxygen contents of the two samples. Table I lists the value of the Néel temperature T_N, the paramagnetic Curie temperature Θ, and the effective moment per vanadium, μ_{eff}, for LaVO₃ as obtained by other workers. The considerable disagreement among various results is thought to be due to differing oxygen contents in the various samples.

Moreover, the values obtained for Θ and μ_{eff} are rather sensitive to the presence of any temperature-independent terms (diamagnetism of the ion cores, χ_{core}, and the Van Vleck susceptibility χ_{VV}, for instance) in the susceptibility. As an example, a Curie-Weiss fit to the raw data, between 350 and 400 K, yields $\Theta = -581$ K and $\mu_{\text{eff}} = 3.33\mu_B$. On the other hand, if we correct the data for χ_{core} [$= -0.66 \times 10^{-4}$ cm³/mol (Ref. 14)] and assume, for the purpose of demonstration, that $\chi_{VV} = 2.1 \times 10^{-4}$ cm³/mol (same as in V₂O₃, which has trivalent vanadium[15]), then a Curie-Weiss fit, between 350 and 400 K, to the corrected data yields $\Theta = -487$ K and $\mu_{\text{eff}} = 3.0\mu_B$, which is closer to the expected value of $2.83\mu_B$ for $S = 1$ and $g = 2$. Hence, in light of the uncertainty in determining the temperature-independent terms in the susceptibility, the values obtained for Θ and μ_{eff} may perhaps not be very meaningful. Our value of T_N is close to that obtained by Zubkov et al.[4] from neutron diffraction.

TABLE I. Values of the Néel temperature T_N, the paramagnetic Curie temperature Θ, and the effective moment per vanadium, μ_{eff}, for LaVO₃ as obtained by other workers.

Reference	T_N (K)	Θ (K)	μ_{eff} (μ_B)
4	144	−665	3.84
6	156	−400	3.07
7	135		
8	<150	−400	2.83
9	137	does not obey Curie-Weiss law	
12	128	−1000	4.2
This work (set 2)	140	see text	see text
This work (set 3)	145	see text	see text

FIG. 2. Measured molar susceptibility χ_M as a function of temperature T for LaVO₃ (a) set 2 and (b) set 3. The susceptibility is measured in a field of 1 T on warming in both field-cooled (FC) and zero-field-cooled (ZFC) cases. The applied field during cooldown is 1 T for the FC curve. (c) The FC data in (b) corrected for χ_{core} and χ_{VV} (see text); the solid line is a Curie-Weiss fit to the data between 350 and 400 K.

magnetic-moment vs applied-field [$M(H)$] isotherms (for ZFC as well as FC cases; see Fig. 3). Shown in Fig. 4 are ZFC isotherms at different temperatures for the $LaVO_3$ sample in set 2. The remanent ferromagnetic moment as deduced from $M(H)$ isotherms is found to go to zero at T_N (Fig. 5). The data in Fig. 5 are for the $LaVO_3$ samples from sets 2 and 3 which had T_N's of 140 and 145 K, respectively. This is consistent with a ferromagnetic component to the spin ordering due to canting of spins and/or due to ferrimagnetism, as will be discussed later. $LaVO_3$ is known to have a structural phase transition, from tetragonal to orthorhombic, near T_N.[6,9,10] We did not observe this transition (see Ref. [16] for details). However, even in a tetragonal structure the point symmetry of the vanadium atoms lacks inversion symmetry. This could give rise to a nonzero Dzyaloshinsky-Moriya[17,18] interaction responsible for the canting of spins. The susceptibility for a system exhibiting canting has been theoretically derived by Moriya.[18] In the vicinity of the Néel temperature, the susceptibility perpendicular to the easy axis (of magnetization) deviates from the Curie-Weiss law and, in the mean-field approximation, is given by

$$\chi_\perp = \frac{N_A \mu_{eff}^2}{3k_B(T+T_N)}\left[\frac{T-T_0}{T-T_N}\right], \tag{1}$$

where N_A is the Avogadro number, μ_{eff} is the effective moment, and k_B the Bohr magneton. T_N is the Néel temperature and is expressed as

$$T_N = \frac{JzS(S+1)}{3k_B}\left[1+\left[\frac{D}{J}\right]^2\right]^{1/2}, \tag{2}$$

$$T_0 = \frac{JzS(S+1)}{3k_B}, \tag{3}$$

where J is the exchange coupling constant, z is the number of nearest neighbors, S is the spin, and D is the Dzyaloshinski-Moriya interaction coupling constant. The susceptibility parallel to the easy axis of magnetization is still given by the Curie-Weiss law. For a polycrystalline sample, the total susceptibility is given by

$$\chi = \tfrac{2}{3}\chi_\perp + \tfrac{1}{3}\chi_\parallel . \tag{4}$$

Clearly, $T_0 < T_N$ from Eqs. (2) and (3), and so we would expect [from Eq. (1)] that near T_N the susceptibility will show a positive deviation from a Curie-Weiss law. However, in fact, we observe a negative deviation from the Curie-Weiss behavior, near the Néel temperature [see Fig. 2 (c)]. Here we have made use of a Curie-Weiss fit between 350 and 400 K, to the susceptibility data corrected for $\chi_{core} = -0.66\times10^{-4}$ cm^3/mol and $\chi_{VV} = 2.1\times10^{-4}$ cm^3/mol, in order to get a value for the paramagnetic Curie temperature and effective moment.

Another mechanism which could give rise to canting is double exchange (discussed by Zener[19]). Double exchange (between V^{4+} and V^{3+} via O^{2-}) favors a ferromagnetic alignment of the spins, whereas in the case of $LaVO_3$ superexchange gives rise to antiferromagnetism. An equilibrium configuration of spins is therefore canted.

The implications of double exchange on various properties were discussed by de Gennes.[20] However, the susceptibility in such a situation is expected to show a second anomaly below T_N, at which point it diverges. Such behavior has been observed in CrSb doped with MnSb.[21]

It is seen from the FC isotherm (Fig. 3) that in low fields the sample exhibits a diamagnetic moment. The slope of the isotherms is, however, paramagnetic (positive) in the complete field range (see Fig. 6). In fact, the susceptibility below T_N and in low fields is found to be negative (see Fig. 7). This is obviously due to the fact that we have taken the susceptibility to be M/H, and this is certainly not appropriate (especially in low fields) when the $M(H)$ isotherm is shifted from the origin. The diamagnetism observed in this compound is quite similar to that seen in ferrimagnetic spinels, such as Co_2VO_4 (Ref. 22) and Co_2TiO_4 (Ref. 23), where there are two sublattices (antiferromagnetically aligned) with ions in crystallographically inequivalent positions, and a spontaneous magnetization results from the incomplete cancellation of the magnetic moments of the two sublattices. The spontaneous magnetization is a sum of the magnetizations of each sublattice, and a sign reversal of the net magnetiza-
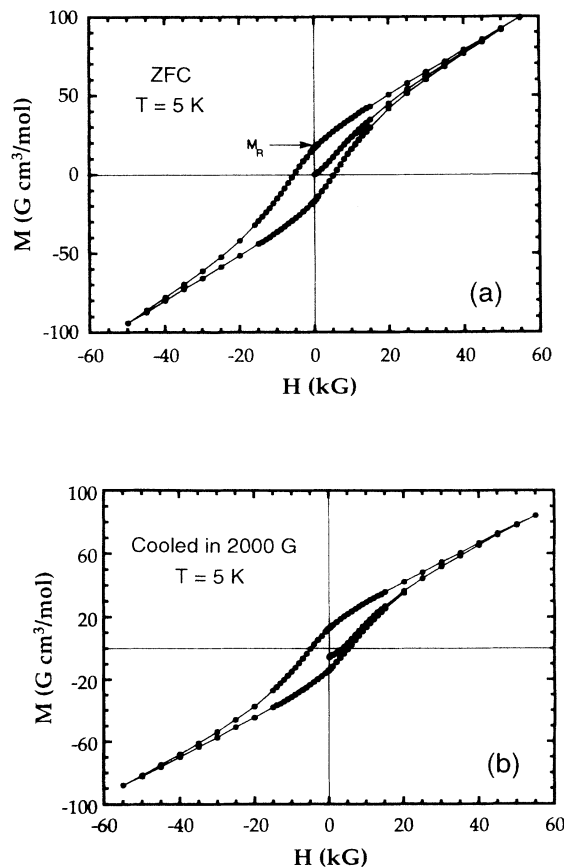

FIG. 3. Magnetization vs field $M(H)$ hysteresis curve for $LaVO_3$ (set 3) for (a) a zero-field-cooled sample (ZFC) at 5 K and (b) a sample that was cooled from 200 to 5 K in a field of 2000 G (FC).

tion could occur because of different temperature dependences of the individual sublattice magnetizations. In the case of LaVO₃, some of the vanadium ions may be magnetically inequivalent, perhaps as a result of V^{4+} ions and/or the presence of crystallographically (slightly) inequivalent sites for the vanadium (which might give rise to different extents of quenching of the orbital magnetic moment and make them magnetically inequivalent), and this might give rise to the diamagnetism observed. As seen in Fig. 6(a), if the sample is cooled in 1 T then the remanent

magnetic moment in zero field is positive (although, if the sample is cooled in lower field, the remanent moment in zero field is negative). This is because a field of 1 T is presumably able to overcome the anisotropy and hence rotate the weak ferromagnetic moment in the direction of the applied field. The corresponding field required to rotate the moments is somewhat higher for the set 2 sample [see Fig. 6(b)]. On the other hand, the remanent moment for a ZFC sample is zero presumably because the different (weakly) ferromagnetic domains are oriented so
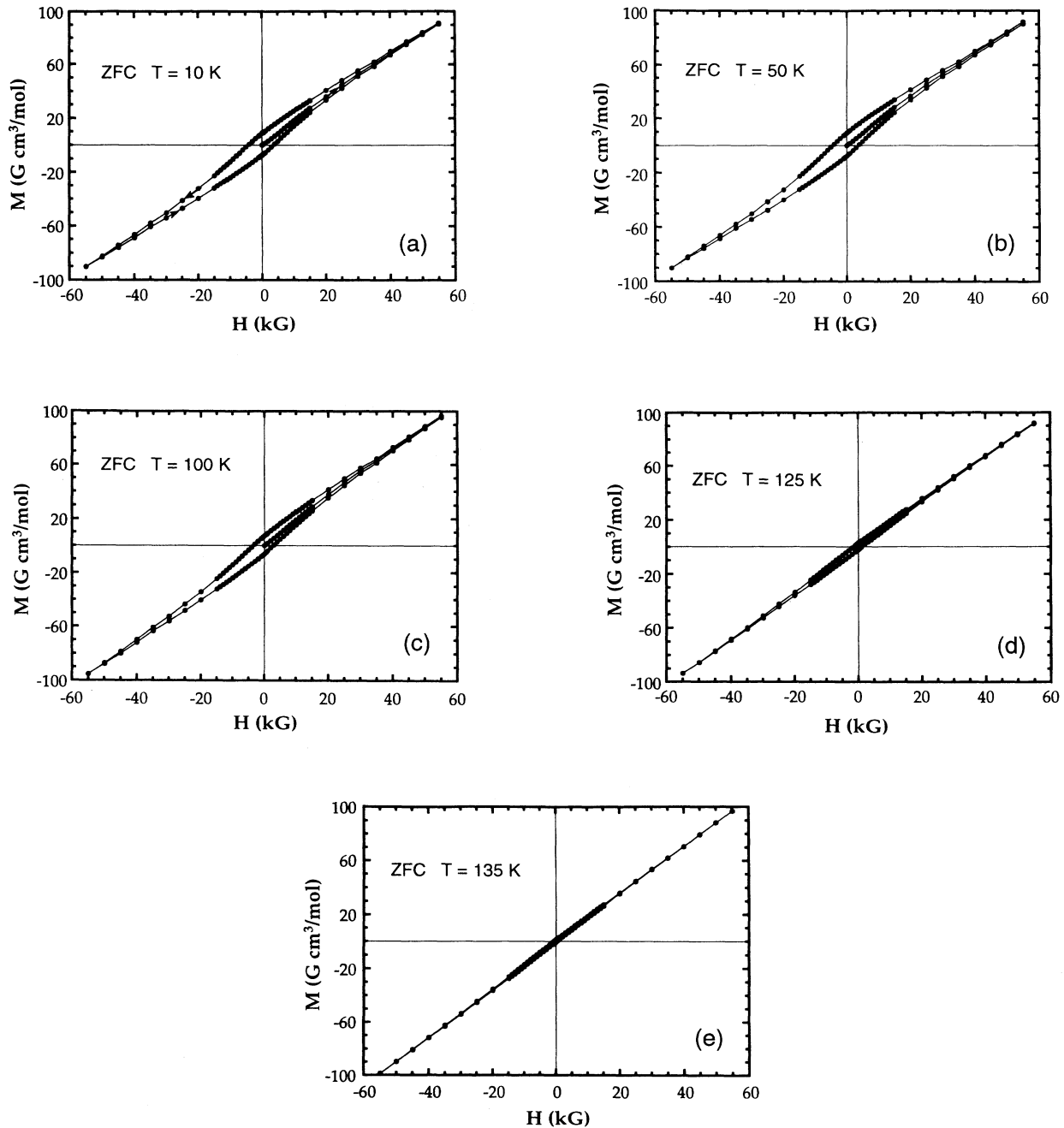

FIG. 4. Magnetization vs field $M(H)$ hysteresis curve for LaVO₃ (set 2) for zero-field-cooled (ZFC) experiments at (a) 10 K, (b) 50 K, (c) 100 K, (d) 125 K, and (e) 135 K.
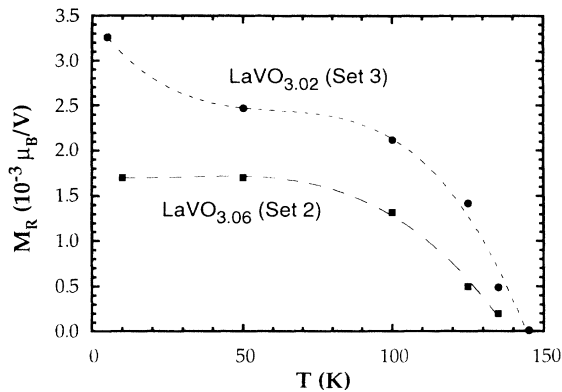
MAHAJAN, JOHNSTON, TORGESON, AND BORSA

FIG. 5. Remanent magnetization M_R as a function of the temperature T for $LaVO_3$ (sets 2 and 3) as obtained from $M(H)$ isotherms at different temperatures. The dashed lines are drawn as guides to the eye.
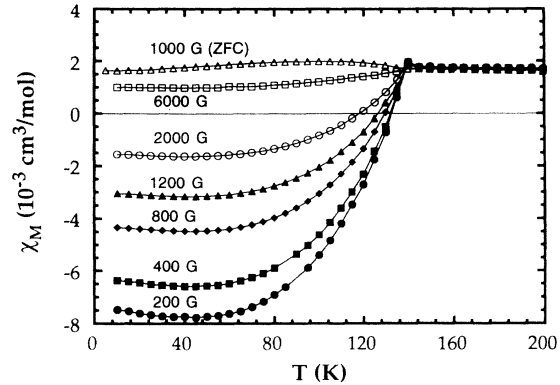
as to give a zero net magnetic moment (to minimize energy).

We performed resistivity measurements on $LaVO_3$ under various conditions of cooling and applied field (Fig. 8). It is seen that, unlike the susceptibility, the resistivity

FIG. 6. Magnetization vs field $M(H)$ hysteresis curves for $LaVO_3$ under different cooling fields at 5 K: (a) set 2 and (b) set 3.

FIG. 7. Molar susceptibility χ_M as a function of the temperature T for $LaVO_3$ (set 3), as measured on warming, after being cooled from 200 K in the indicated magnetic field, except for the 1000-G (ZFC) data, in which case the sample was zero field cooled and then measured on warming in 1000 G.

is rather immune to whether the sample is zero field cooled or not. We do not see any transition to zero resistance at the temperature at which the susceptibility in Fig. 7 becomes diamagnetic.

C. ^{51}V NMR

The ^{51}V NMR signal (as seen by the cw spectrometer) is very broad even at room temperature [Fig. 9(a)]. The resonance linewidth shows critical broadening [Fig. 9(b)] as one approaches the antiferromagnetic ordering temperature, typical of paramagnets (insulators). The signal disappears below T_N since the internal field shifts the resonance beyond the region of experiment. The disappearance of the signal is generally considered a sign of magnetic ordering. The ^{51}V Knight shift (paramagnetic shift) is -0.6%. We were unable to see this signal at room
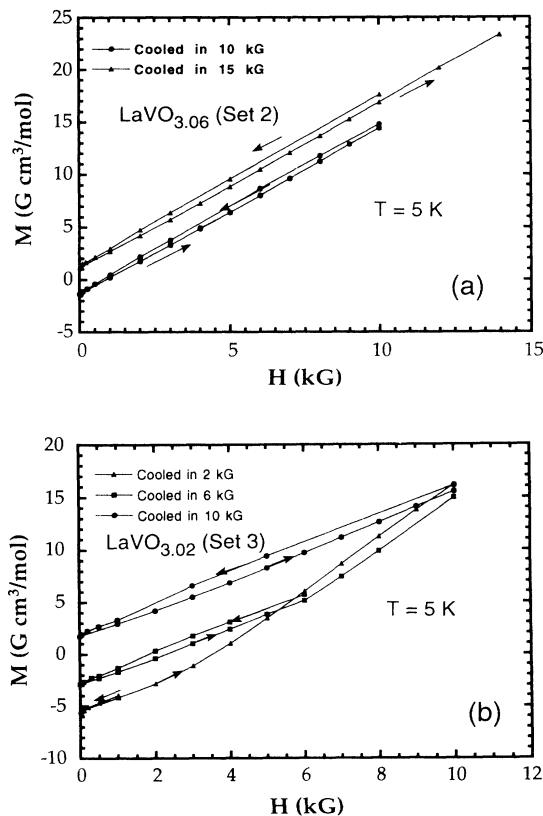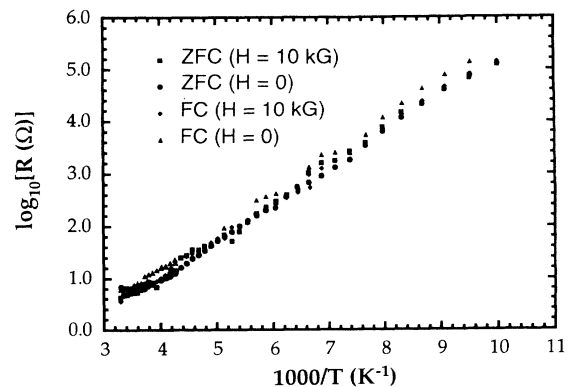

FIG. 8. Logarithm of the resistance $\log_{10}(R)$ as a function of $1000/T$ [for $LaVO_3$ (set 2)], where T is the temperature, under the following conditions: zero field cooled and measured in zero applied field [ZFC ($H=0$)], zero field cooled and measured in an applied field of 1 T [ZFC ($H=10$ kG)], field cooled in 1 T and measured in zero applied field [FC ($H=0$)], and field cooled and measured in an applied field of 1 T [FC ($H=10$ kG)].
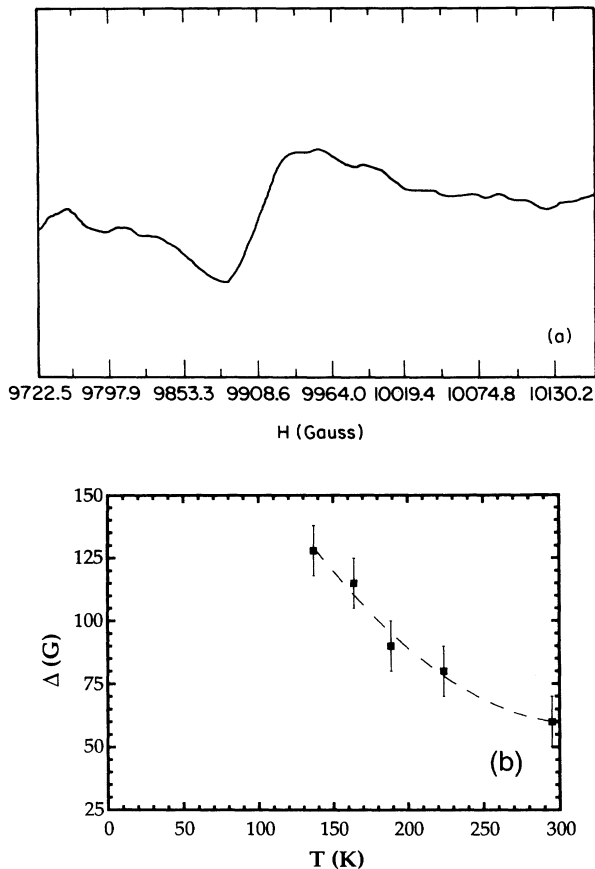
FIG. 9. (a) ^{51}V NMR line shape for LaVO$_3$ (set 2) obtained in a cw experiment at room temperature with a modulating field (peak to peak) of 16 G and (b) ^{51}V NMR linewidth Δ as a function of the temperature T for LaVO$_3$ (set 2). The dashed line is drawn as a guide to the eye.

FIG. 10. Amplitude of the spin echo as a function of the frequency for LaVO$_3$ (set 3) in a field of 5.892 T at two different temperatures.

temperature by the pulse method. This would appear to be due to a very short T_2 (spin-spin relaxation time) due to strong fluctuating local moments bringing about rapid deexcitation of the nuclei from the excited state to the ground state. However, we have observed a signal with a shift of $\approx +0.07\%$ in a field of 5.892 T by the pulse method (Fig. 10). The signal persists below T_N, and the frequency shift and the resonance linewidth (as obtained by plotting the amplitude of the spin echo as a function of frequency) are independent of temperature. These results indicate that the signal most probably originates from an impurity phase, even though our x-ray-analysis measurements showed no evidence for any impurity phases; thus, the impurity-phase concentration would have to be below our x-ray-analysis detection limit ($\sim 5\%$).

IV. CONCLUSIONS

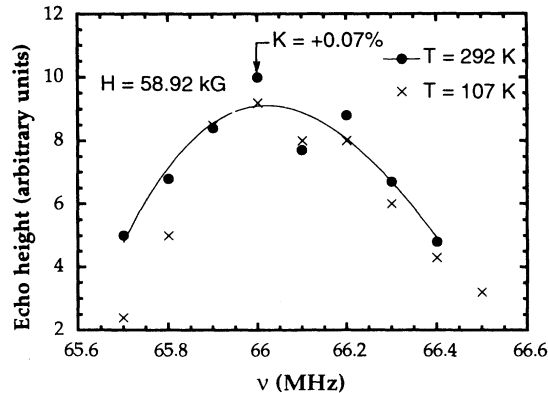The compound LaVO$_3$ is found to be a tetragonal distortion of the cubic perovskite structure at room temper-

ature. TGA measurements evidence the formation of a stoichiometric compound.

We have observed a negative magnetic moment (in low fields) for LaVO$_3$ in a field-cooled experiment. Also seen is hysteresis in $M(H)$ isotherms below the Néel temperature for ZFC as well as FC cases. The hysteresis and diamagnetism appear to be associated with ferrimagnetism in this compound.

We have observed ^{51}V NMR by the cw method, and the NMR measurements confirm the association of the peak in the susceptibility with magnetic ordering. An additional broad signal with a positive shift was observed by the pulse method, the origin of which is perhaps due to V^{4+} ions in impurity phases.

Toward the end of our investigations, the results of a magnetization study on LaVO$_3$ appeared.[24] These results are in general agreement with our magnetization measurements. These authors independently found the large diamagnetic susceptibility ($=M/H$) after field-cooling the compound below T_N ($H = 500-2000$ Oe) and noted a small ($\simeq -0.001\mu_B$/formula unit) negative remanent moment when the field was turned off below T_N; however, the material was not characterized via $M(H)$ isotherms as we have done. In addition, x-ray-diffraction data are presented in Ref. 24 which demonstrate that a pseudo-cubic to orthorhombic structural phase transition occurs near T_N in their sample.

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