Anomalous magnetoresistance in high-temperature organic-based magnetic semiconducting $V(TCNE)_x$ films

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Anomalous positive magnetoresistance (MR) in high temperature organic-based magnet $V(TCNE)_x$ (TCNE= tetracynoethylene) thin films is reported. MR increases linearly with applied magnetic field and shows a maximum at the ferrimagnetic ordering temperature. The suggested roles of oppositely spin polarized π^* electronic subbands and magnetization fluctuations due to the disordered nature of $V(TCNE)_x$ films are discussed. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1556120]

I. INTRODUCTION

There has been much progress in the field of spintronics in the recent past with the development of new types of devices that exploit both electric and spin properties of the charge carriers in a material (e.g., spin valves, high speed magnetic sensors, spin light emitting diodes, etc.). For example, spin polarized electronic transport gives rise to the giant (negative) magnetoresistance (GMR) effect in multilayers incorporating transition- or rare-earth metals.[1] Here we report anomalous positive magnetoresistance to high magnetic fields (9 T) for organic-based ferrimagnetic semiconductor $V(TCNE)_x$ ($x\sim2$) thin films with a T_c up to ~400 K (TCNE= tetracynoethylene).[2,3] Magnetoresistance (MR) was proposed to arise in $V(TCNE)_x$ due to spin polarization which is a required property for spintronics applications.[3]

Organic-based magnets were first reported in the mid 1980s with the discovery of ferromagnetism below an ordering temperature of 4.8 K in the linear chain electron transfer salt $[FeCp_2^*][TCNE]$ (Cp^* = pentamethylcyclopendienide).[4] $V(TCNE)_x$ with T_c up to 400 K has a room temperature resistivity, ρ, of $\sim10^4$ Ω cm.[5] $V(TCNE)_x$ films with different T_c's can be prepared by the chemical vapor deposition (CVD) method by varying preparatory conditions and annealing temperatures.[6] Based on x-ray photoemission spectroscopy and saturation magnetization studies, V^{II} has a spin $S=3/2$ and $[TCNE]^-$ has $S=1/2$ with one unpaired electron in the π^* orbital.[2] The observed saturation moment of $\sim1\ \mu_B$ per $V(TCNE)_2$ unit results from the antiparallel alignment of one V^{II} ($S=3/2$) and two $[TCNE]^-$ radicals ($S=1/2$ each).[6,7] In this study we used three different films referred to as samples A, B, and C with T_c's of >350, ~275, and ~235 K, respectively. We show that the MR is anomalous, with MR proportional to H below T_c and proportional to H^2 above T_c. The proposed origin of this phenomenon in spin polarization of the conduction and valence "bands" is discussed.

II. EXPERIMENTAL DETAILS

For resistance measurements, gold contacts of 40 nm thickness were deposited onto a glass substrate and $V(TCNE)_x$ films were deposited on top of these contacts using a gas phase reaction of TCNE and $V(CO)_6$.[2] The typical thickness of these films is ~1–5 μm depending upon deposition time and distance from the reaction zone. These air sensitive films are handled in inert atmosphere throughout. Samples were sealed in a sample holder after making electrical connection to the gold contact pads. Films show a resistance of a few MΩ at room temperature. The four-probe resistance method was used when possible; the two-probe method was employed when the resistance of the films increases to very large values (at low temperatures). The two methods show the same resistance values in the overlapping region. The ferrimagnetic resonance (FMR) measurements were performed on a commercial Bruker Instruments ESP300 (*X*-band) ESR spectrometer using a TE_{102} resonant cavity. Sample temperature was varied in the range 10–300 K using an Oxford 900 continuous flow helium cryostat.

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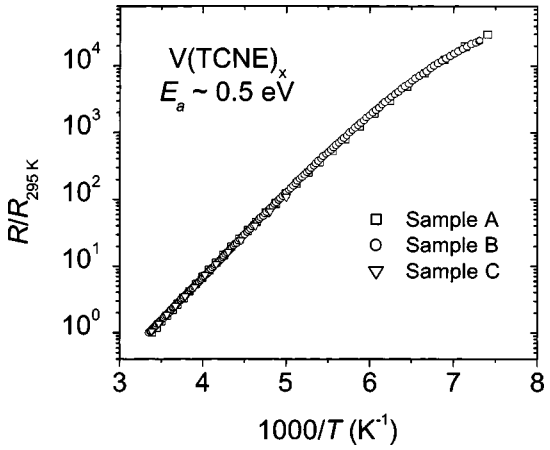

FIG. 1. Normalized resistance vs inverse temperature for samples A ($T_c > 350$ K), B ($T_c \sim 275$ K), and C ($T_c \sim 235$ K).

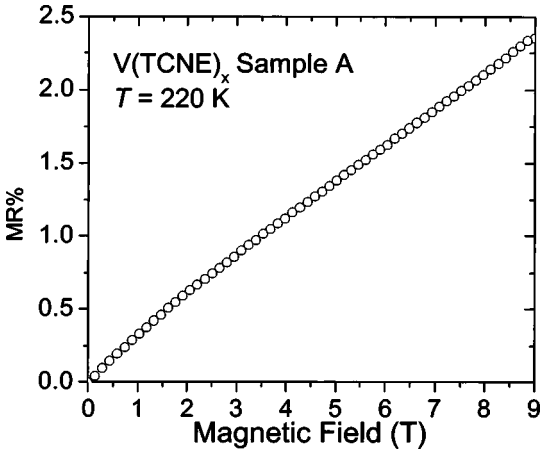

FIG. 3. MR against field in the range 0–9 T for sample A at 220 K. T_c of sample A>350 K.

III. RESULTS

Normalized resistances as a function of inverse temperature for samples A ($T_c > 350$ K), B ($T_c \sim 275$ K), and C ($T_c \sim 235$ K) are shown in Fig. 1 on a semilog plot. The three samples show nearly identical temperature dependencies of normalized resistance despite their different T_c's and different room temperature resistivities (ρ_{RT} resistivity values for samples A, B, and C are $\sim 3.5\times 10^4$, $\sim 1.4\times 10^5$, and $\sim 5.3\times 10^6$ Ω cm, respectively).

A typical MR variation with applied magnetic field is shown in Fig. 2 for sample C below its $T_c \sim 235$ K. MR percentage is defined as

$$\mathrm{MR}\% = 100[\rho(H)-\rho(0)]/\rho(0).$$

In the paramagnetic state for sample C at 297 K, MR(H) increases quadratically at low fields and with a modest linear contribution at higher fields. For sample C at 225 K (in the ferrimagnetic state) MR(H) is linear in the entire field range (0–0.6 T) studied. MR(H,T) behaviors with the plane of the film parallel and perpendicular to the external field are found to be identical.

The MR of sample B ($T_c \sim 275$ K) also was measured in the 0–0.6 T range and it has similar linear MR(H) behavior below T_c, but MR(H) well above T_c was not studied for this sample due to instrumental limitations.

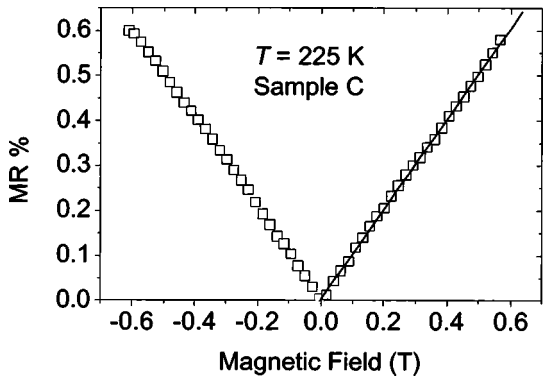

FIG. 2. Field dependence of MR for sample C at 225 K. T_c of sample C is ~ 235 K.

Sample A has a T_c that exceeds the decomposition temperature (>350 K) from an extrapolation of temperature dependence of the magnetization. The MR for sample A was extended to 9 T; a typical MR vs H plot is given in Fig. 3 for $T = 220$ K. This sample also shows a linear MR behavior beginning from very low fields. The slope is reduced slightly around 1.5 T and the MR continues to increase linearly up to 9 T with no sign of saturation. The change in slope in MR(H) at 1.5 T correlated with the change in magnetization versus field at about 1 T as M(H) approaches saturation.[6]

Figures 4(a)–4(c) represent the temperature dependence of MR% at 0.6 T and ferrimagnetic resonance (FMR) intensity for the samples A ($T_c > 350$ K), B ($T_c \sim 275$ K), and C ($T_c \sim 235$ K), respectively. The FMR intensity is proportional to the magnetization of the sample and magnetic ordering temperature can be determined from the spontaneous rise in magnetization. T_c's for sample B and C are ~ 275 and ~ 235 K, respectively. For samples B and C the MR exhibits a broad maximum at T_c, decreasing slowly above and below the T_c. Sample A displays no maximum as its T_c is well above the temperature region explored.

IV. DISCUSSION

Preliminary MR results of V(TCNE)$_x$ recently have been reported.[3] From the Arrhenius type behavior between 180 and 300 K the activation energy, E_a, was determined to be ~ 0.5 eV. The activation behavior is associated with thermal activation of charge carriers in the Coulomb energy split π^* band.[3] The charge transport involves hopping among $[\mathrm{TCNE}]^-$'s. The single occupied molecular orbital of each $[\mathrm{TCNE}]^-$ can accept a second electron with opposite spin with an additional Coulomb repulsion U_c. Therefore the activation energy, 0.5 eV, is a measure of the effective U_c.

The Hubbard model[8] with nearly half-filling provides a relevant description of $[\mathrm{TCNE}]^-$ electronic states. The π^* band of $[\mathrm{TCNE}]^-$ is split into two nonoverlapping subbands provided $U_c \gg t$, where t is the electronic transfer-integral between neighboring $[\mathrm{TCNE}]^-$'s. The spins of electrons in the lower filled Hubbard subband should have antiferromag-

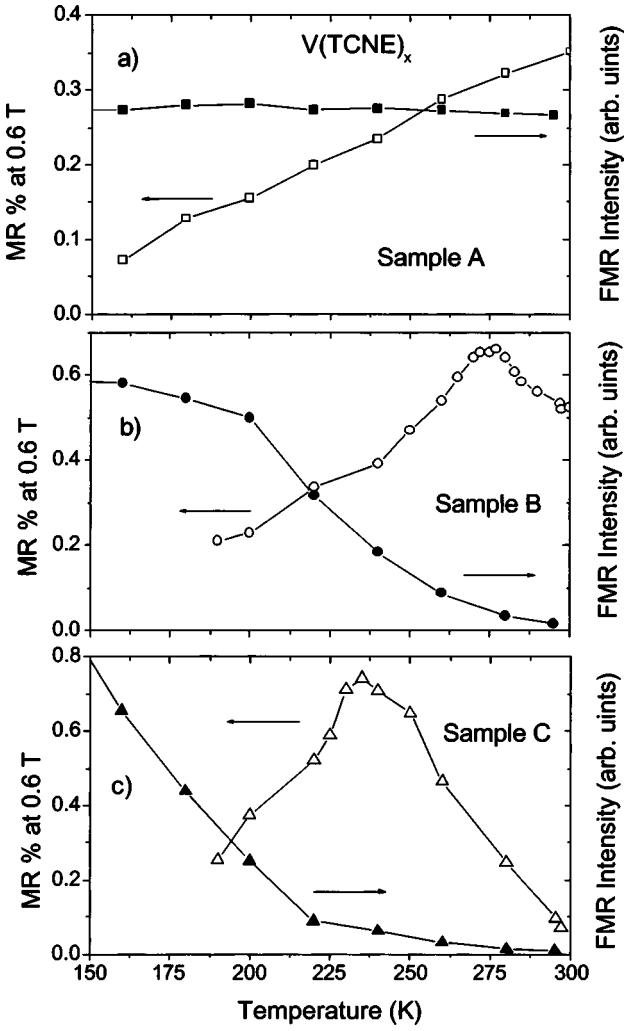

FIG. 4. The variation of MR and ferrimagnetic resonance intensity with temperature for (a) sample A, (b) sample B, and (c) sample C.

netic order with corresponding exchange constant $J' = 2t^2/U_c$. If this were the case the saturation magnetization M_s of $V(TCNE)_x$ should correspond to net spin 3/2. Experimentally M_s corresponds to net spin 1/2 supporting the antiparallel arrangement of V^{II} spin and $[TCNE]^-$ spin. If $J' \ll J$ (J' being the exchange constant between two $[TCNE]^-$'s and J between V^{II} and $[TCNE]^-$), then in the ordered state the electronic spins of the lower subband are parallel. Application of an external magnetic field increases the energy gap ΔE (which is approximated as $\Delta E = U_c + 4J\langle S\rangle\langle\sigma\rangle$, where $\langle S\rangle$ and $\langle\sigma\rangle$ correspond to the spin polarization of V^{II} and lower π^* subbands, respectively) and leads to a linear increase in the positive MR. As temperature is lowered the influence of the external magnetic field becomes less effective due to the development of stronger internal magnetic fields and hence the MR decreases. A quadratic MR behavior in the paramagnetic region, a maximum in the MR near T_c, and a linear MR response below T_c were accounted for on the basis of this model.[3]

Anomalous positive MR was reported for thin films of the high resistivity ($>10^9\ \Omega$ cm) ferromagnetic semiconductor $Eu_{1-x}Sm_xO$.[9–11] These data were explained using a model based on the scattering of free charge carriers by ferromagnetic clusters of the rare earth ions. In contrast to the rare earth clusters of $Eu_{1-x}Sm_xO$, in $V(TCNE)_x$ the V^{II} ion is coordinated with the large $[TCNE]^-$ radical ions and thus makes the application of this scattering model unlikely in the $V(TCNE)_x$ case.

In summary, a large positive MR has been observed in the organic-based room temperature ferrimagnetic semiconductor $V(TCNE)_x$. The linear ($T < T_c$) and quadratic ($T \gg T_c$) results have been analyzed in terms of spin polarized subbands formed by the π^* band of $[TCNE]^-$. Spin polarization is essential for incorporating these organic-based magnets in spintronics devices. The spin polarization of mobile charges in $V(TCNE)_x$ may enable their use in organic-based spintronics devices.

ACKNOWLEDGMENTS

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