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High field linear magnetoresistance in fully spin-polarized high-temperature organic-based ferrimagnetic semiconductor V(TCNE)$_x$ films, $x \sim 2$

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ABSTRACT

Positive magnetoresistance (MR) has been observed to increase linearly up to 32 T in the magnetically ordered state of organic-based ferrimagnetic semiconductor V(TCNE)$_x$ films ($x \sim 2$; TCNE = tetracyanoethylene) with T_c above room temperature (> 350 K). In this material conductivity takes place via electrons activated from 3d level of V^{2+} to upper π^* subband of [TCNE]$^{\bullet-}$. We show an unusual MR behavior without any sign of saturation up to a magnetic field of 32 T. For temperatures less than T_c MR exhibits a linear behavior in the entire field range and above T_c it has a quadratic dependence at low fields. Temperature and field dependent behaviors of MR in this material are explained on the basis of spin polarizations in V^{2+} 3d level and the upper π^* subband of [TCNE]$^{\bullet-}$ formed by Coulomb repulsion.

1. Introduction

Spintronics has been a very active field of research in the recent past [1]. It creates additional functionalities to conventional electronics by exploiting both charge and spin degrees of freedom of the current carriers. For example, spin-valve read head sensors rapidly increased the areal density of magnetic recording information storage devices [2]. Presently intense research work is in progress to extend the use of spin property of charge carriers not only for storage of information but also for processing of it [3]. Spin injection is one of the crucial aspects for realizing spintronic devices. Ferromagnetic metals can supply polarized spins but it is difficult to achieve efficient spin injection from ferromagnetic metals into semiconductors due to the conductivity mismatch between them [4–6]. Availability of FM semiconductors for use as spin injectors would reduce the conduction mismatch problem.

Temperature and field dependencies of anomalous positive magnetoresistance (MR) were reported for three V(TCNE)$_x$ films, with different T_c's, in modest external magnetic fields up to 0.6 T [7]. MR showed a quadratic variation with applied magnetic field above the T_c and a linear response below the T_c. For one of the samples magnetic field was extended to 9 T and its MR increased linearly with no sign of saturation. Further, the variation of MR (recorded at an applied field of 0.6 T) with temperature exhibits a maximum near the T_c. These behaviors were consistently observed for all the three samples investigated. These anomalous and large MR behaviors are discussed in terms of spin polarization in the frontier energy bands of V[TCNE]$_x$ [8]. In this work we have extended the applied magnetic fields to very high fields (up to 32 T) and observed an extraordinary linear MR behavior up to the highest magnetic field in the temperature range below T_c. Before presenting this high field work we summarize the recent literature on V[TCNE]$_x$ concerning spintronics.

There is an extensive activity in developing a variety of new materials for spintronics. Different types of inorganic materials being explored include manganites, spinel ferrites, double perovskites, and dilute magnetic semiconductors (DMS) [9]. Substantial progress has been made in the area of DMS based on the so-called III–V compounds GaAs and InAs doped with Mn at low concentrations. Annealed $Ga_{1-x}Mn_xAs$ samples have T_c as large as 173 K [10] and for well prepared heterostructures T_c was reported as high as ~250 K [11]. GaN and ZnO have been reported to main-

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tain ferromagnetism above room temperature by proper Mn doping [12].

There is a growing interest in the development of organic-based magnetic and non-magnetic materials for use in spintronics devices. Organic-based magnets could provide an alternative pathway in achieving novel characteristics of spintronic materials with tunable magnetic and electronic properties via organic methodologies. This class of magnets was first reported in 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, TCNE = tetracyanoethylene) [13]. Magnetic ordering at above room temperature (>350 K) was achieved in $V(TCNE)_x \cdot y$ S powders ($x \sim 2$; $y \sim 0.5$; solvent S = CH_2Cl_2) [14] and in $V(TCNE)_x$ ($x \sim 2$) films grown by chemical vapor deposition (CVD) in the absence of any solvent [15]. Experimentally observed saturation magnetization is in accordance with V^{2+} with spin $S = (3/2)$ and $[TCNE]^{\bullet -}$ with $S = (1/2)$ align antiferromagnetically resulting in a net spin $S = (1/2)$ per formula unit [14]. In the same family of compounds, $Mn(TCNE)_x$ and $Fe(TCNE)_x$ have T_c's of ~ 75 and ~100 K, respectively. Recent reports of photo-induced magnetism in solution-prepared $Mn(TCNE)_x \cdot yCH_2Cl_2$ powder material, [16] and photoinduced magnetic and electrical phenomena in solvent-free $V(TCNE)_x$ films [17] signify the importance of these materials in both basic and applied research.

Spin density distribution in $[TCNE]^-$, a key component of several molecule-based magnets, was experimentally determined by polarized neutron diffraction studies of tetra-n-butylammonium tetracyanoethenide $[Bu_4N]^+[TCNE]^-$ [18,19]. These studies showed that the spin on the $[TCNE]^-$ was not completely localized on the sp^2 carbon atoms but distributed across the radical anion. This technique was applied to determine the spin density in $[FeCp_2^*]^+$ as well and to explain the ferromagnetic interactions inside the $[FeCp_2^*]^+[TCNE]^-$ chains [20]. Recently, quantum chemical calculations were reported on the electron affinity and spin density of TCNE, hexacyanobutadiene (HBCD) and their anionic radicals [21]. These calculations of neutral and reduced TCNE compare well with the earlier experimentally observed spin density distribution.

Due to the lack of long-range structural order in $V(TCNE)_x$, X-ray absorption techniques were employed to obtain local electronic and structural information [22,23]. Both X-ray photo electron spectroscopy (XPS) and extended X-ray absorption fine structure (EXAFS) studies indicate that V has an oxidation state of about 2+ and the V ions are coordinated by six N ions, most likely in a slightly distorted octahedral environment.

Ferrimagnetic resonance (FMR) studies were reported for $V(TCNE)_x$ in the form of powder samples prepared in solution of CH_3CN [24] and also in the form of thin films grown by chemical vapor deposition (CVD) in the absence of any solution [25]. FMR analyses indicate lesser structural and magnetic disorder in thin films compared to powder samples.

Recently, X-ray magnetic circular dichroism (XMCD) and a suite of X-ray absorption techniques were employed to probe the magnetic state and electronic structure, respectively [26,28]. XAS and MCD results were attributed to bonding and backbonding interactions in $V(TCNE)_x$ which explain its novel electronic properties [26]. A large XMCD signal, which is proportional to the magnetic moment on the vanadium ions, shows that the $V(TCNE)_x$ films are magnetically ordered at room temperature. A combination of valence band photoelectron spectroscopy (PES) and resonant photoemission (RPE) data suggests that the highest occupied electronic state in this material is V(3d) derived [27,28]. This experimentally implied position of V(3d) valence band modifies the earlier assumption that the LUMO π^* band of $[TCNE]^{\bullet -}$ split into two subbands, as in the Hubbard model with nearly half-filling, giving rise to valence and conduction bands [8]. We will return to this when we discuss magnetoresistance data.

Very recently, theoretical studies have been reported on different physical properties of $V(TCNE)_x$ [29,30]. A model of $V(TCNE)_x$ was proposed based on the experimental inputs and simulated structural, electronic, and magnetic properties using hybrid exchange functional theory [29]. These computational results are in confirmation with a fully spin-polarized half-semiconductor ground state earlier proposed by Prigodin et al. [8]

2. Experimental

For electrical resistance measurements, gold contacts were deposited onto a glass substrate and $V(TCNE)_x$ films were deposited on top of these contacts by chemical vapor deposition (CVD) method as described in Ref. [15]. 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. High field MR measurements in the temperature range 150–300 K were performed using dc resistive magnet facilities at National High Magnetic Field Laboratory (NHMFL) at Tallahassee, Florida. The dc magnetization was measured using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, San Diego) in the temperature range 5–300 K.

3. Results and discussion

We describe here results for films that were prepared under slightly different controlled CVD preparatory conditions. Selected examples of these films are referred to here as samples 1 and 2 with T_c s of ~280 K and ~275 K, respectively. The dc magnetization of sample 1, measured at an applied field of 0.01 T, as a function of temperature (Fig. 1) reveals a magnetic ordering temperature of ~ 280 K with the onset of spontaneous magnetization.

Normalized electrical resistivity vs. temperature behavior is displayed in Fig. 2 on a semilog plot for samples 1 and 2 of $V(TCNE)_x$. The nearly identical behaviors of normalized resistivities confirm an earlier report [7]. The resistivity data between 290 and 220 K obey the Arrhenius-type activation law giving an activation energy, E_a, of 0.52(3) eV which is in excellent agreement with the literature value [7,8]. Even though the resistivity data seemed to fit well in the entire temperature range to Mott's 3D variable range hopping (VRH) model, the values obtained for number density of states, $N(E_F)$, are not meaningful [8].

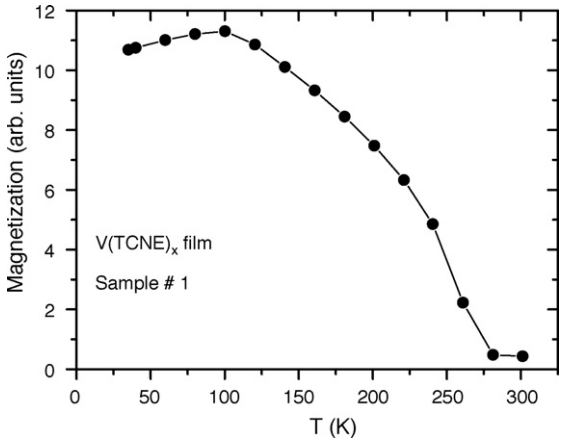

Fig. 1. Typical temperature dependence of zero field cooled magnetization for $V(TCNE)_x$ measured at an applied field of 10 mT.