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Ferrimagnetic Resonance of High- T_c Organic-Based Magnet $V[TCNE]_x$ ($x \approx 2$) Films

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Designing spintronics materials with high T_c is a big challenge in the modern nanomaterials' research. $V[TCNE]_x$ is considered to be an excellent candidate for spintronics applications with some advanced properties. Ferrimagnetic resonance (FMR) of three high- T_c organic-based magnetic $V[TCNE]_x$ films is reported. These samples prepared by chemical vapour deposition (CVD) method under different preparatory conditions have different transition temperatures: > 300 K (sample A), 280 K (sample B), and 220 K (sample C). Their different magnetic parameters such as effective magnetization, full width at half maximum, *etc.* have being studied in the temperature range 10–300 K. Sample A shows long-range ordered magnetic behaviour, while samples B and C exhibit spin-glass-like behaviour.

Проектування матеріалів для спінтроніки з високим T_c є великою проблемою в сучасних дослідженнях наноматеріалів. $V[TCNE]_x$ вважається чудовим кандидатом для застосувань у спінтроніці з деякими розширеними властивостями. Повідомляється про феримагнетний резонанс (FMR) трьох високотемпературних магнетних плівок $V[TCNE]_x$ на органічній основі. Ці зразки, приготовані методом хемічного осадження пари (CVD), в різних підготовчих умовах мають різні температури переходу:

> 300 K (зразок А), 280 K (зразок В) і 220 K (зразок С). Їхні різні магнетні параметри, такі як ефективна намагнетованість, повна ширина в половині максимуму тощо, вивчалися в діапазоні температур 10–300 K. Зразок А демонструє магнетну поведінку дальнього діапазону, тоді як зразки В і С демонструють схожість на поведінку спін-скла.

Key words: ferrimagnetics, spintronics, EPR spectroscopy, magnetization dynamics, surface magnetic properties.

Ключові слова: феримагнетики, спінтроніка, ЕПР-спектроскопія, динаміка намагнетованости, поверхневі магнетні властивості.

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I. INTRODUCTION

V[TCNE]_x (TCNE = tetracyanoethylene) films (room temperature organic-based magnet) attracts a lot of attention from scientists nowadays. It is being reported spin-valve working at room temperature using V[TCNE]_x as the spin injector/detector [1]. These films exhibit a large positive magnetoresistance (MR) with the maximum at the ferrimagnetic ordering temperature [2]. The spin polarization of mobile charges in V[TCNE]_x makes it potentially good for spintronics usage at different temperatures. Among the large number of organic-based magnets, V[TCNE]_x is especially unique, because it has the highest magnetic-ordering temperature: $T_c \cong 400$ K [3]. Another advantage of V[TCNE]_x films is the possibility to tune their T_c by changing preparatory conditions; for example, by oxidation of vanadium or by thermal treatment [4]. In our work, we consider three different films: sample A with $T_c > 300$ K, sample B with $T_g = 280$ K, and sample C with $T_g = 220$ K. V[TCNE]_x molecule consists of V²⁺ with spin $S = 3/2$ and two [TCNE]^{•-} with spin $S = 1/2$ (one unpaired electron in the π^* orbital). Because of antiparallel alignment of V²⁺ ions and [TCNE]^{•-} radicals, we can observe saturation moment of approximately $1\mu_B$ per each V[TCNE]₂ [5].

We use FMR as a very powerful technique to study magnetization dynamics and surface magnetic properties of V[TCNE]_x films [6]. Due to this study, we have a view of the magnetic structure of the film samples on the microscopic level with very high resolution and sensitivity. In this work, we do emphasis on the correlation between the magnetic-ordering temperature and the magnetic properties of studied films together with the structures of the three samples, which were thoroughly examined. The obtained results are important for further magnetotransport analysis and for use of studied films in spintronics devices.

FMR studies of thin CVD films of V[TCNE]_x have already been reported by Plachy *et al.* Those films have several advantages: FMR exhibits very narrow linewidths near T_c ; the temperature dependence of the

FMR as a function of the orientation of film provides an accurate measure of the anisotropy field; measurements of the FMR intensities and line widths give estimates of the porosity of the films; the occurrence of spin waves provides an estimate of the exchange stiffness constant [7].

II. EXPERIMENTAL

$V[TCNE]_x$ films were of different thickness: 4 microns for sample A, 2 microns for sample B, and 6 microns for sample C. They were deposited on the glass substrates at room temperature by means of the CVD method. The process of preparation of the samples was performed in the glove box and described in details in Ref. [4]. After that, samples were sealed in special ESR-grade quartz tubes. The FMR experimental measurements were made by using commercial Bruker Instruments ESP 300 (X-band) EPR spectrometer equipped by TE_{102} resonant cavity. For temperature measurements in the range of 10–300 K, the Oxford 900 continuous flow helium cryostat had being used.

III. RESULTS AND DISCUSSION

In Figure 1, the temperature dependence of absorption intensity, which is proportional to magnetization, is shown for three samples. The onset temperature of spontaneous magnetization in each case is directly related to the ferromagnetic ordering temperature of each sample. We recorded FMR spectra at different angles between the plane of film and applied magnetic field, θ : 0° , 30° , 60° , and 90° . Such spectra are shown in Fig. 2, *a*, *b*, *c* for samples A, B, and C, respectively. As the angle θ increases, the resonant field is also increases as we expect for thin films because of the demagnetization effect.

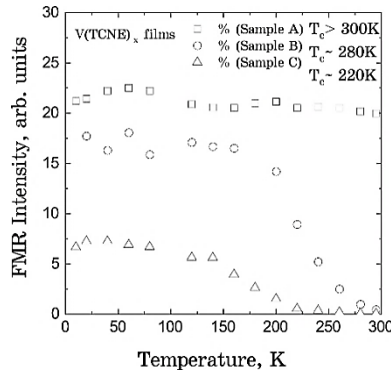


Fig. 1. Magnetization as a function of temperature for samples A, B, and C obtained by double integrating the FMR derivative absorption curves.

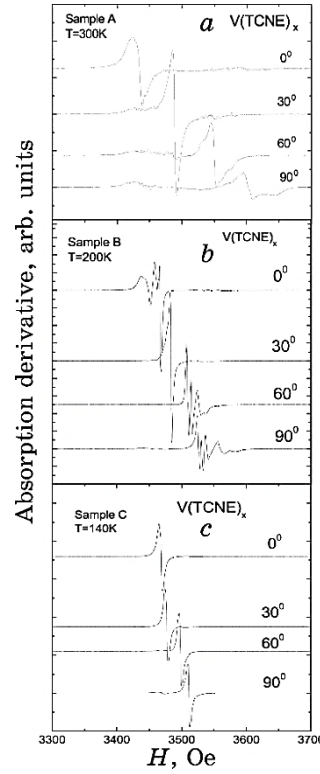


Fig. 2. *a, b, c*. FMR spectra for samples A, B, and C, respectively, at different angles between the plane of film and applied field.

For the given radio frequency, we can write such formulas for the film sample for the parallel and perpendicular resonance fields:

$$H_{\parallel}^{\text{res}} = (\omega/\gamma) - 2\pi M_{\text{eff}}, \quad (1)$$

$$H_{\perp}^{\text{res}} = (\omega/\gamma) + 4\pi M_{\text{eff}}. \quad (2)$$

From formulas (1) and (2), we can get value of effective magnetization:

$$M_{\text{eff}} = (H_{\perp}^{\text{res}} - H_{\parallel}^{\text{res}})/(6\pi). \quad (3)$$

The angular dependence of ferromagnetic resonance field is shown in Fig. 3, *a, b, c* for sample A, B, and C, respectively. The data are similar to the results reported by Plachy *et al.* [7]. These data were fit using the resonance frequency condition for samples with small anisotropy given by [8]

$$(\omega/\gamma)^2 = (H_r + 4\pi M_{\text{eff}} \cos 2\theta)(H_r - 4\pi M_{\text{eff}} \sin^2 \theta), \quad (4)$$

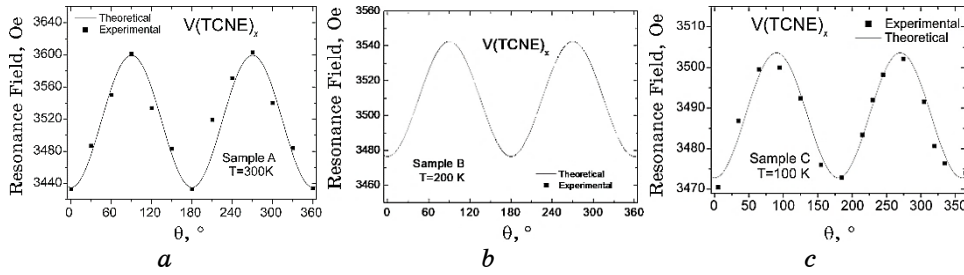


Fig. 3. *a, b, c.* The theoretical and experimental FMR field H_r against angle θ between plane of film and applied field.

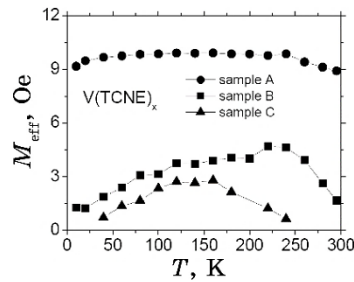


Fig. 4. Temperature dependence of effective magnetization, M_{eff} . M_{eff} is determined from the resonance fields in the parallel and perpendicular configurations.

where ω is the radio frequency, γ is the gyromagnetic ratio (2.80 GHz/kOe), H_r —FMR field, θ —angle between the plane of film and applied magnetic field, and M_{eff} —the effective magnetization of the sample. It is assumed, of course, that the directions of magnetization are coincident with the applied field \mathbf{H} .

A look at the FMR spectra of sample B (Fig. 2, *b*) reveals that the sample has several domains (inhomogeneous regions) with different magnetization. Same we can say about sample A (Fig. 2, *a*) as many small resonance spectra are superimposing main broad peak. It also has to be mentioned that complexity of the spectra is very sensitive to the angle θ . Similar spectra got Plachy *et al.* in Ref. [7].

In Figure 4, M_{eff} is shown for all three samples as a function of temperature, found from the resonance fields in the parallel and perpendicular configurations. For sample A, we got an almost constant M_{eff} in the whole temperature range 10–300 K. For sample B and C, M_{eff} increases with decrease in temperature, then reaches maxima (at ≈ 230 K and ≈ 130 K, respectively), and then decreases when temperature down to 10 K. Such temperature variations of M_{eff} demonstrate that the sample A has long-range magnetic-order behaviour, and both samples

B and C have spin-glass-like ordering behaviour. The difference in behaviour of samples B and C compared to sample A together with reduced transition temperatures related to the fact of having more structural disorder.

Figure 5 displays temperature variations of line widths (full width at half maximum) for angle 45° for all samples. At angle 45° , the complexity of the spectra is minimal. The line shape is almost Lorentzian in the entire temperature range for all three samples indicating that electron exchange in the samples is three-dimensional, and that the relaxation processes are mainly responsible for the width of the lines.

Line widths of samples A and B increase monotonically as the temperature goes down. Samples A and B have rather small line width at room temperature, sample C has rather large FWHM at room temperature compare with two other samples. At lowest measured temperature (10 K), the line width of all three samples is almost same. The temperature dependence of FWHM for sample C is very similar to previously reported powder sample $V[TCNE]_x$, which had $T_c = 160$ K [9].

Becker made a special model and calculated EPR-line width for spin-glasses with anisotropy. According to him, in case of no remnant magnetization in the system, the line width is given by the formula [9, 10]:

$$\Delta H = \frac{ABT}{B^2 + T^2}, \quad (5)$$

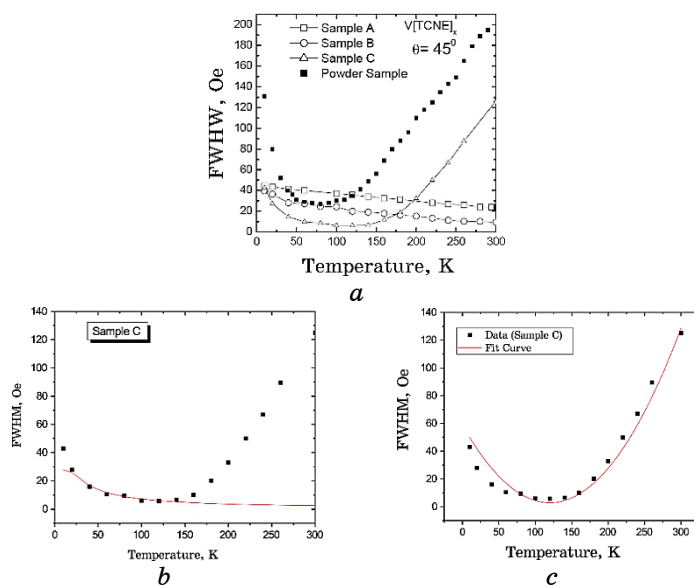


Fig. 5. FMR linewidth (full width at half maximum—FWHM) as a function of temperature.

where $A = g\mu_B K / (h\omega\chi)$ and $B = M_2 / (Kk_B\omega)$, K is the anisotropy constant, M_2 is constant related to spin relaxation; g —Landé factor, h is Planck's constant; μ_B —Bohr magneton; χ —static transverse susceptibility; ω is the frequency of microwaves.

By doing fit analysis of the data in Fig. 5 (fit curve is shown in Fig. 5, *a*) by above formulae, in our case, we have values for parameters A and B of 46 Oe and 6.8 K, respectively. For the previously reported sample, they were 309 Oe and 5.5 K, respectively. One conclusion we can make is that the anisotropy in the film is much smaller than in the powder sample.

We can also do fit analysis of our data for resonance field (Fig. 6) by using formulae for the resonance field for the region of temperatures below T_c [9]:

$$H_{\text{res}} = H_0 + \frac{AT^2}{B^2 + T^2}, \quad (6)$$

where $H_0 = h\omega / (g\mu_B)$, A and B are same as in formulae (5). Parameters A and B found from fit analysis of the resonant field are not same as found from data for the line width at low temperatures. For parameters A and B , we have values 34 Oe and 83.1 K, respectively (fit curve is shown in Fig. 6, *a*). This non-standard behaviour of physical parameters at low temperatures makes research of the samples at the low and very low temperatures interesting for further studies.

According to Long, for temperatures $T \cong T_c$, we have a critical regime given by the formulae [9]:

$$\Delta H = a_0 + b' \left| \frac{T}{T_{\text{min}}} - 1 \right|^n, \quad (7)$$

where a_0 is the residual line width, and T_{min} is the temperature of the

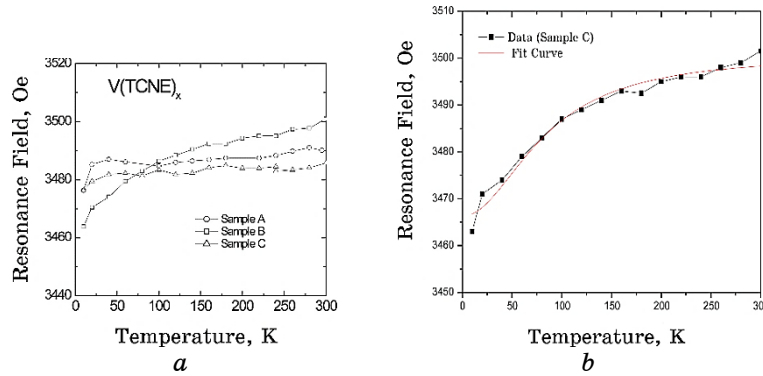


Fig. 6. Temperature variation of FMR field.

minimum line width. The exponent n shows the disorder of the system. In our study, it has the value of 2.1 (fit curve is shown in Fig. 5, b), which is close to 2.0 reported before.

For $T \gg T_c$, we have thermal broadening regime [9]:

$$\Delta H = (a_0 - b\theta) + bT, \quad (8)$$

where a_0 is the residual linewidth, θ —the Curie–Weiss temperature, b is thermal broadening constant. Regime of thermal broadening can be observed only for sample C. For samples A and B, we do not observe regime of thermal broadening because temperature range is short.

IV. CONCLUSIONS

It was shown the consistence of the Becker model with respect to the $V[\text{TCNE}]_x$ films at different temperature regimes. The angular-dependence of the EPR data is in the perfect agreement with the theory. Based on the spectra, we know a lot about the structures of the films and many parameters as functions of temperature. Discrepancies in fitting parameters at low temperatures are pushing forward to the further research at very low temperatures. Obtained data are coincided with the data of Plachy *et al.* very well especially for resonant field.

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