phys. stat. sol. (a) **196**, No. 1, 240–243 (2003) / **DOI** 10.1002/pssa.200306396

New magnetic phenomena in vanadium hexacyanochromates

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Received 1 July 2002, accepted 15 October 2002

PACS 75.30.Cr, 75.50.Gg, 75.50.Xx

Magnetic properties of Prussian blue analogues $V^{III}[Cr^{III}(CN)_6] \cdot 7H_2O$ and $(V^{IV}O)_3[Cr^{III}(CN)_6]_2 \cdot 4H_2O$ are presented. $M(T)$ dependence shows an increase of magnetisation below the paramagnetic Curie temperature T_{cp} = 107 K and T_{cp} = 167 K for the complexes with V^{IV} and with V^{III}, respectively. Both compounds are ordered ferrimagnetically below the Curie temperature T_c = 53 K (V^{IV}) and T_c = 88 K (V^{III}) determined by the Weiss method from M^2 vs. T dependence. Experimentally found $\mu_s = 0.\ 63\mu_B$ (V^{IV}) and $\mu_s = 0.\ 91\mu_B$ (V^{III}) corresponds well with the theoretical one. The irreversibility in FC and ZFC magnetisation was observed. The maxima in $M(T)$ at T_{max} = 16 K (sample V^{IV}) and at T_{max} = 32 K (sample V^{III}) at H = 10 Oe shift to lower temperatures and become less pronounced at higher magnetic fields. The H-dependence T_{max} and bifurcation T_{irr} suggests a cluster glass behaviour. Both samples exhibit a strong electron paramagnetic resonance signal at $g(V^{III})$ = 1.84 and $g(V^{IV})$ = 1.79 with the peak to peak linewidth $\Delta H_{pp}(V^{III})$ = 73 Oe and $\Delta H_{pp}(V^{IV})$ = 944 Oe at room temperature.

1. Introduction Prussian blue is sometimes considered as the first coordination compound. Analogues of Prussian blue revealed in the last few years as very flexible molecular precursors to build three-dimensional molecule-based magnets with tuneable and high Curie temperature, T_c, or to grow high nuclearity clusters with tuneable high spins and anisotropy. The Curie temperature was pushed from T_c = 5.6 K in the Prussian blue itself to room temperature in vanadium−chromium Prussian blue analogues [1]. In this family of materials the Currie temperature varies between T_c = 115 K in a vanadium-chromium ferrimagnet containing vanadium (IV) [2] and T_c = 315 K in a sample with vanadium (II) and vanadium (III) [3]. In our paper we report on magnetic properties of two compounds $V^{III}[Cr^{III}(CN)_6] \cdot 7\ H_2O$ and $(V^{IV}O)_3[Cr^{III}(CN)_6]_2 \cdot 4\ H_2O$. In our knowledge there was no study of the irreversibility in zero-field-cooling and field-cooling magnetisation on the vanadium hexacyanochromates that is why we paid a special attention to study of this phenomenon.

2. Experimental The sample containing V^{III} was synthesised by mixing of $K_3[Cr(CN)_6]$ with VCl_3 under anaerobic condition. The sample containing V^{IV} was prepared by the similar way under aerobic conditions. The number of water molecules in the crystal structure was determined from TGA measure-

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0031-8965/03/19603-0240 $ 17.50+.50/0

ments. X-ray diffraction patterns showed amorphous crystal structure of the sample with V^{III} and cubic crystal structure with lattice parameter a = 1.0377(11) nm of the sample containing V^{IV}. Details of the synthesis, characterisation and crystal structure determination are presented in [4]. EPR measurements were performed by ERS 200 spectrometer. Both samples exhibit a strong paramagnetic resonance signal at $g(V^{III}) = 1.84$ and $g(V^{IV}) = 1.79$ with the peak to peak linewidth $\Delta H_{pp}(V^{III}) = 73$ Oe and $\Delta H_{pp}(V^{IV}) = 944$ Oe at room temperature. Magnetic properties were studied in the temperature range 4.2 K $\le T \le$ 300 K and in magnetic fields 10 Oe $\le H \le$ 50 kOe using a SQUID magnetometer.

3. Results and discussion The temperature dependence of the inverse susceptibility, measured on both samples in magnetic field $H = 500$ Oe, is shown in Fig. 1. Paramagnetic part of the $1/\chi$ versus T curve is not field dependent and similar parabolic decrease can be obtained also at $H = 10$ Oe. Only upper part, above $T = 250$ K , of the V^{IV} curve obeys a simple Curie-Weis law with $\mu_{eff} = 2.87\mu_B$ and $\Theta = -24$ K, suggesting a ferrimagnetic ordering. An intersection of parabolic fit to high temperature data with zero line represents a paramagnetic Curie temperature, T_{cp}. The value of $T_{cp} = 107$ K of V^{IV} sample corresponds very well with the Curie temperature $T_c = 115$ K determined a similar way [2]. The relationship between the critical temperature, T_c, the number of magnetic nearest neighbours, z, and the exchange parameter, J, can be analysed in the frame of molecular field theory. The Curie temperature $T_c = 199$ K estimated by this concept for $V^{III}[Cr^{III}(CN)_6]$ compound [2] is a little bit higher than our paramagnetic Curie temperature $T_{cp} = 167$ K of the V^{III} sample. The lower value of T_{cp} can be attributed to partial oxidation of V^{III} to V^{IV}. The ferrimagnetic Curie temperature $T_c = 53$ K of sample V^{IV} and $T_c = 88$ K of sample V^{III} have been determined by a classical Weiss method from $M^2(T)$ as it is shown in the inset of Fig. 1.

The magnetisation curves of both samples show steep increase of magnetisation at low fields, do not show pronounced hysteresis behaviour and do not saturate up to $H = 50$ kOe (Fig. 2). The value of saturated magnetic moment $\mu_s = 0.63\mu_B$ at $T = 46$ K for V^{IV} sample and $\mu_s = 0.91\mu_B$ at $T = 4.5$ K for V^{III} sample has been determined from $M(1/H)$ curve as it is shown in the inset of Fig. 2. Experimentally found μ_s corresponds well with theoretical one, $\mu_s^{teor} = gJ(V^{IV}) - gJ(Cr^{III}) = 1.55 - 0.77 = 0.78\mu_B$ for V^{IV} sample and $\mu_s^{teor} = gJ(V^{III}) - gJ(Cr^{III}) = 1.63 - 0.77 = 0.86\mu_B$ for V^{III} sample, obtained under assumption that magnetic moments on V and Cr couple antiferromagnetically.

The magnetisation versus temperature curves at $H \le 500$ Oe are displayed in Fig. 3. The magnetisation of sample V^{III} increases slowly below $T = 190$ K with a deviation from a parabolic increase between

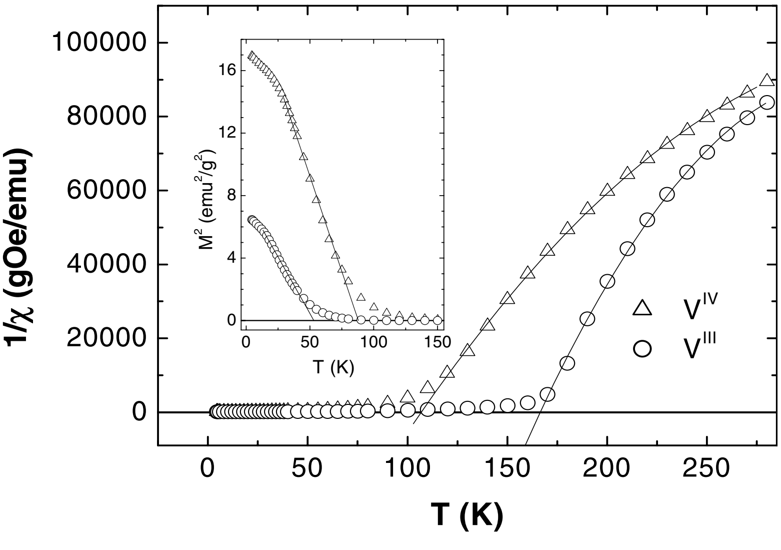

Fig. 1 Inverse susceptibility at $H = 500$ Oe plotted versus temperature. Inset shows a determination of the Curie temperature by Weiss method from $M^2(T)$ at $H = 500$ Oe.

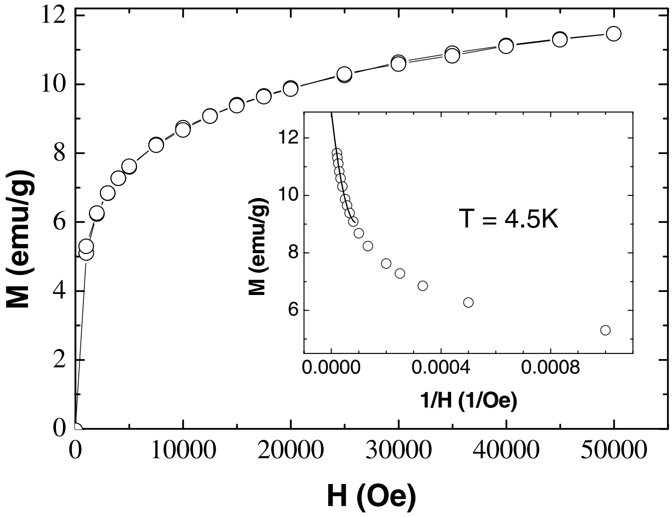

Fig. 2 Magnetisation versus magnetic field measured on the sample with V^{III}. Inset shows a determination of the saturated magnetic moment.

100 K < T < 190 K, and reaches a maximum below T = 50 K. Such a slow increase can be attributed to the size and size distribution of particles in the sample and/or the presence of a second phase with V^{IV}. $M(T)$ curves of V^{IV} sample are shown in the inset of Fig. 3. $M(T)$ dependence behaves similarly as for V^{III} sample only characteristic temperatures are sifted to lower temperature; the increase of magnetisation starts below T = 120 K and appearance of a maximum below T = 30 K. The increase of magnetisation is smooth and comparable with FC curve published in [2].

Magnetisation shows irreversibility in ZFC and FC curves with the temperature of bifurcation ranging from T_{irr} = 35 K at H = 10 Oe to T_{irr} = 10 K at H = 500 Oe for sample V^{III}, and T_{irr} = 17 K at H = 10 Oe to T_{irr} = 8 K at H = 500 Oe for sample V^{IV}. The characteristic feature of $M(T)$ curves, the maximum, shifts to lower temperature with applied magnetic field from T_{max}= 30K at H = 10 Oe to T_{max} = 10 K at H = 500 Oe for sample V^{III}, and T_{max}= 17.5 K at H = 10 Oe to T_{max} = 10 K at H = 500 Oe for sample V^{IV}. The appearance of a maximum is a characteristic feature of spin glasses (SG). The field dependence of T_{irr} and T_{max} is in contrast with canonical SG and can be attributed to cluster glass behaviour. Such behaviour was found on different analogues of Prussian blue [5–7].

Real part χ' of AC susceptibility at H = 1.4 Oe measured on the sample containing V^{III}, shown in Fig. 4, follows DC magnetisation measurements with increase of susceptibility below T = 190 K and a

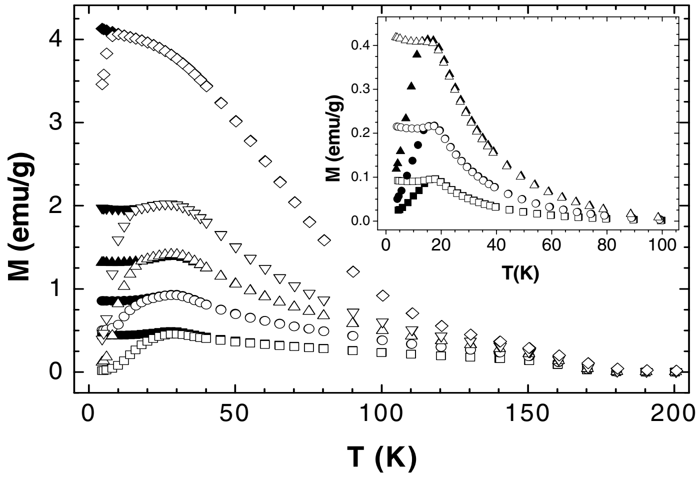

Fig. 3 ZFC (open symbols) and FC (solid symbols) curves for V^{III} sample measured at fields H = 10 Oe, 25 Oe, 50 Oe, 100 Oe and 500 Oe. Inset displays the same curves for V^{IV} sample measured at fields H = 10 Oe, 25 Oe, 50 Oe.

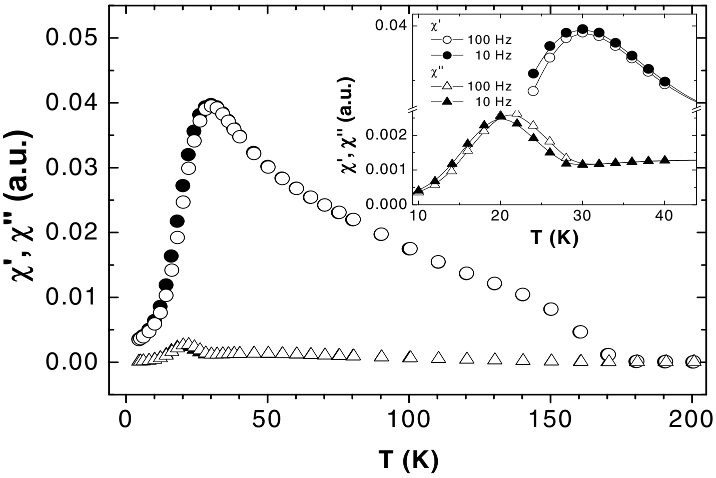

Fig. 4 AC susceptibility measured at H = 1.4 Oe on the V^{III} sample. Inset shows a maximum of real and imaginary part of the complex susceptibility.

maximum at about $T = 30$ K. The imaginary part of complex susceptibility χ'' increases below $T = 170$ K reaches a maximum at about $T = 45$ K, local minimum at $T = 30$ K, corresponding to maximum in χ', and another maximum at $T = 22$ K. The real part and the imaginary part of the complex susceptibility are only slightly frequency dependent and the peak is shifted to higher temperature – see inset of Fig. 4. This feature is more pronounced in the case of χ''. Frequency dependence of the complex susceptibility, which characterises cluster glass systems, were also observed in [6, 7].

Acknowledgement Our work was partially supported by VEGA grant 1168.

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