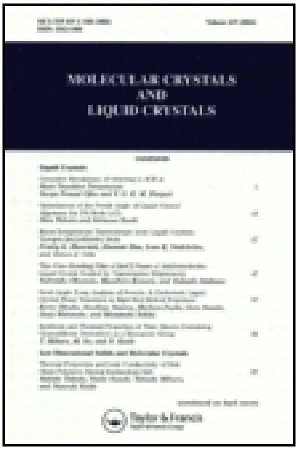

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A Study of the Magnetic Ordering in $KCo[Fe(CN)_6]{\bullet}xH_2O$

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The results of the ac susceptibility and dc magnetization in the wide range of temperatures are presented for $KCo[Fe(CN)_6]{\bullet}xH_2O$. Magnetic ordering was revealed at T = 13.2 K. Frequency dependence of the complex susceptibility and non-linear response suggest glassy like behavior.

Keywords: spin glass; magnetic susceptibility; cyanometallates

INTRODUCTION

The magnetic properties of the compounds from the hexametallates family $A_nM[M'(CN)_6]{\cdot}xH_2O$, where A is alkali metal ion and M and M' are transition metal cations are extensively studied over the last decade[1,2]. Table I shows the collection of the recent results of the studies on the hexacyanometallates family. The crystal structure of these compounds is very simple[3]: fcc lattice of M ions is shifted by ½ ½ ½ from another fcc lattice of M' ions. The M' ions are octahedrally surrounded by C atoms while M ions are surrounded by N atoms respectively. M-C≡N-M' chains form three dimensional network. Due to the different local crystal field the M ions are in the high spin state while M' ions in the low spin state. It is generally accepted that the mechanism of the magnetic ordering in cyanometallates comes from the superexchange involving CN ligands orbitals. If the two transition metal ions are in the orthogonal states there is a ferromagnetic coupling between them. If the two ions M and M' are in the non-orthogonal magnetic state, coupling between the two is usually antiferromagnetic.

TABLE I Critical temperatures for cyanometallates

compound	T_c[K]	reference
$K_2Mn^{II}[Mn^{II}(CN)_6]$	41	[4]
$Mn_3^{II}[Mn^{III}(CN)_6]_2 \cdot 12H_2O$	37	[4]
$CsMn^{II}[Mn^{III}(CN)_6] \cdot ½ H_2O$	31	[4]
$Cs_2Mn^{II}[V^{II}(CN)_6]$	125	[5]
$CsNi^{II}[Cr^{III}(CN)_6] \cdot 2 H_2O$	90	[6]
$Cr_3^{II} [Cr^{III}(CN)_6]_2 \cdot 10H_2O$	240	[7]
$Cs_{0.75}Cr_{1.25}^{II}[Cr^{III}(CN)_6] \cdot 5 H_2O$	190	[7]
$V_{0.42}^{II}V_{0.58}^{III}[Cr^{III}(CN)_6]_{0.86} \cdot 2.8H_2O$	315	[8]
$Mn^{II}[Mn^{IV}(CN)_6] \cdot 1.14H_2O$	48.7	[9]

Our study was devoted to $KCo^{II}[Fe^{III}(CN)_6] \cdot xH_2O$. One can expect ferrimagnetic order of Co^{2+} (S=3/2) and Fe^{3+} (S=1/2) ions.

RESULTS

$KCo^{II}[Fe^{III}(CN)_6] \cdot xH_2O$ was prepared by adding 100 cm^3 of 0.1M $Co(NO_3)_2$ aqueous solution to the 50 cm^3 of 0.1M $K_3[Fe(CN)_6)]$ solution. An amorphous precipitate of $KCo^{II}[Fe^{III}(CN)_6] \cdot xH_2O$ was paper filtered and washed several times with distilled water. After this the precipitate was dried in 25°C, granulated, washed again and dried. The sample in the form of dark, very fine powder and mass ca. 0.1 g was used.

$KCo^{II}[Fe^{III}(CN)_6] \cdot xH_2O$ has magnetic phase transition at 13.2 K, below this temperature there is a magnetic order. Figure 1 shows magnetization as a function of external magnetic field at T = 4.2 K. The inset displays the hysteresis loop at the same temperature. The coercive field is H_c = 930 Oe and the remnant magnetization M_r = 2800 cm^{3}G/mol. These values are relatively large in compare to the other cyanometallates. One can see that with our magnetic field of 56 kOe we are still far from saturation.

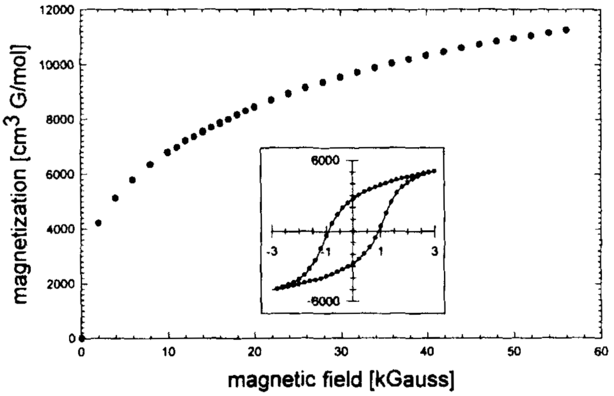

FIGURE 1 Magnetization as a function of magnetic field at 4.2 K. Inset shows hysteresis loop in the same units.

Figure 2 shows complex susceptibility as a function of temperature for five different frequencies. Both the real and imaginary parts of the susceptibility show maximum at 13.2 K. Above this temperature the susceptibility does not depend on the frequency. Below 13 K both parts of complex susceptibility depend on the frequency. The position of the maximum however does not change with frequency. When the susceptibility measurement are performed in external dc magnetic field the maximum of the anomaly moves towards lower temperatures and its intensity decreases. The real part of the complex susceptibility behaves in different way than the imaginary one. Figure 3 shows the dependence of the complex susceptibility at ω = 125 Hz for different magnetic fields. When magnetic field increases the temperature of the maximum in susceptibility decreases indicating that the nature of interaction is antiferromagnetic. It should be noticed that when magnetic field is increased real part of susceptibility shows double maximum structure while the imaginary part of susceptibility has single maximum structure.

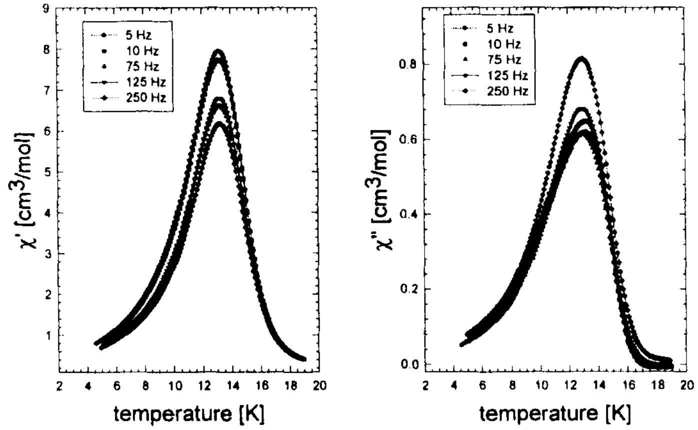

FIGURE 2 Real (left) and imaginary (right) parts of susceptibility

Our experimental setup enables us to study non-linear response to ac field. When the primary coil of the susceptometer is supplied with the frequency ω and at the same time the lock-in amplifier is tuned to the frequency 2ω, 3ω ... the signal observed is proportional to the non-linear susceptibility:

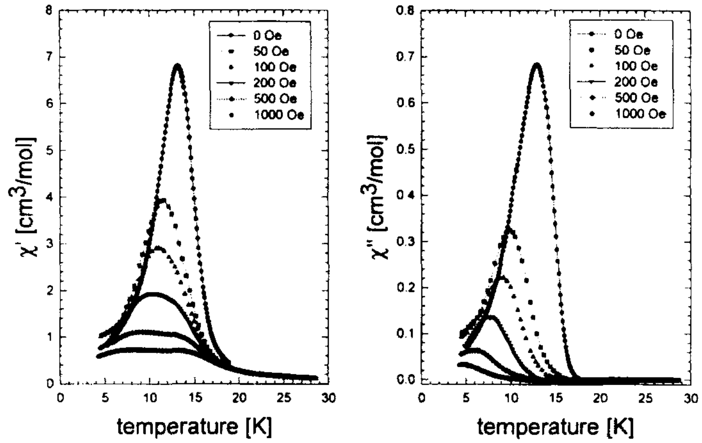

FIGURE 3 Real (left) and imaginary (right) parts of complex susceptibility for f=125 Hz and different dc biased fields

$$M(\omega) = \chi_1(\omega)H_0\cos\omega t + \frac{1}{2}\chi_2(\omega)H_0^2\cos 2\omega t + \frac{1}{4}\chi_3(\omega)H_0^3\cos 3\omega t$$

where M is magnetization, H_0 is the amplitude of ac field, χ_1 is linear and χ_2, χ_3 are non-linear susceptibilities. Figure 4 shows non-linear susceptibilities measured as a function of temperature for five different frequencies. It should be noticed that the non-linear signal is symmetric with the respect to T_c and the critical temperature is 14.2 K, a little higher than the one found from linear susceptibility. The width at the half maximum of the anomaly is about 2 K and should be considered as the critical region. This value is rather large in comparison to the usual spin glasses. It should be mentioned here that the magnitude of the non-linear signal depends on the thermal history and magnetic field of the sample.

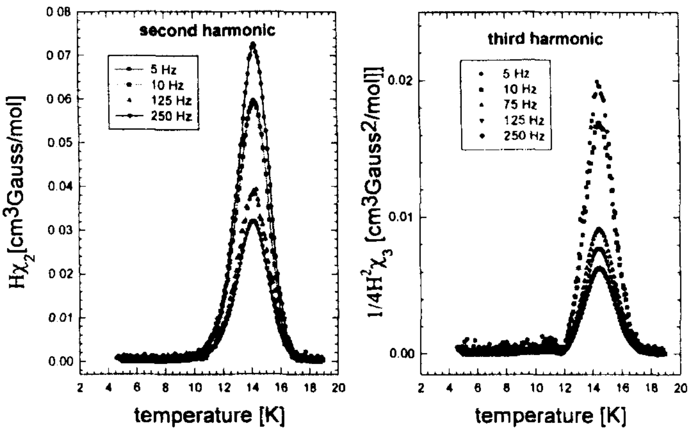

FIGURE 4 Second (left) and third (right) harmonics of non-linear susceptibility

DISCUSSION

Magnetic interactions in cyanometallates are in principle well described by the superexchange mediated by CN bridge[9]. In the present case we are dealing with $^4T_{1g}$ term of Co^{2+} with (t_{2g}, e_{2g}) magnetic orbitals and $^2T_{2g}$ term of Fe^{3+} with t_{2g} magnetic orbital. Due to the non-orthogonality of these states there is an antiferromagnetic coupling between the two magnetic moments which leads to ferrimagnetic order. For spin only moments this should lead to the saturation magnetization of $2\mu_B$ i.e. 11170 cm^3G/mol. Figure 1 shows that with our magnetic field of 56 kOe we are still below the saturation, but the magnetic moment is already above the mentioned value. We believe that it is due to spin orbit coupling. Our earlier studies of high temperature behavior of

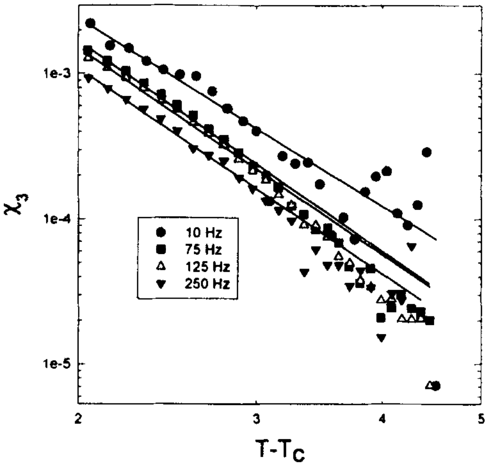

FIGURE 5 Linear fits to log-log plot of third harmonics of non-linear susceptibility

susceptibility[10] also show that the effective moment in paramagnetic region is 20% higher than the spin only value. Frequency dependence of the susceptibility and the irreversible processes observed in magnetization suggest glassy character of the magnetic phase transition. There is certain disorder in the sample due to the fact that only half of the positions are occupied by K ions. Our diffraction patterns and IR absorption spectra show that there is crystalline water in our sample. Due to the above mentioned reasons glassy behavior is not very much surprising. As it is known that at the glass transition non-linear susceptibility χ_3 diverges with critical exponent γ we made the estimation of this exponent in our case. Figure 5 presents non-linear susceptibility χ_3 in the log-log scale for different frequencies. All curves fit very well with exponent $\gamma = -4.7 \pm 0.1$ what is in full agreement with ±J Ising spin glass in d=2[11]. Please note however that we are not able to approach T_c very close due to rounding of the curve.

Acknowledgments
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