MAGNETIC PROPERTIES OF CHAIN-LIKE STRUCTURES BASED ON CU(II) *

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The study of magnetic properties of the polymeric compounds $Cu(C_2H_8N_2)_2Ni(CN)_4$, $Cu(C_2H_8N_2)_2Ag_2(CN)_4$ and $Cu(C_{10}H_8N_2)_2Ag_2(CN)_4.H_2O$ is the main purpose of this work. Magnetization measurements at 4.2 K in fields up to 6 T confirmed assumptions on weak exchange interactions, resulting from the knowledge of a crystal structure. Specific heat studies performed in the temperature range 50 mK-1.5 K revealed phase transitions into the long-range-order in milikelvin region in all compounds. The deviations from assumed chain-like behaviour are discussed.

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1 Introduction

Theoretical investigations of easy-plane Heisenberg chains in magnetic fields applied parallel to the hard axis have revealed the existence of non-linear excitations governing non-linear spin dynamics of the studied systems [1, 2]. Specific heat contribution of these excitations was theoretically estimated in [1]. This theoretical effort has stimulated our study of three polymeric compounds $Cu(en)_2Ni(CN)_4$ (I), $Cu(en)_2Ag_2(CN)_4$ (II) and $Cu(bpy)_2Ag_2(CN)_4.H_2O$ (III) (en=$C_2H_8N_2$, bpy=$C_{10}H_8N_2$) to find a well defined one-dimensional S =1/2 Heisenberg system with a weak anisotropy - a suitable candidate for the investigations of the non-linear excitations.

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Since Cu(II) ion is a typical Heisenberg ion displaying a relatively weak magnetic anisotropy, our attention has been focused on the title compounds exhibiting quasi-one-dimensional crystal structure in which only Cu(II) ion is responsible for the magnetic properties of the studied compounds since the square-planar nickel(II) ion in the $[Ni(CN)_4]^{2-}$ group is diamagnetic. The structure of $Cu(en)_2Ni(CN)_4$ is built up of electroneutral [-CN-Cu(en)$_2$-NC-Ni(CN)$_2$-CN-] chains while the structure of $Cu(bpy)_2Ag_2(CN)_4.H_2O$ and $Cu(en)_2Ag_2(CN)_4$ consists of positively charged chains [-Cu(bpy)$_2$-NC-Ag-CN-]$^+$ and [-Cu(en)$_2$-NC-Ag-CN-]$^+$, respectively, and isolated $[Ag(CN)_2]^{2-}$ anions. Furthermore, $Cu(bpy)_2Ag_2(CN)_4.H_2O$ containes non-coordinated water molecules. Some of intermolecular distances indicate the formation of hydrogen bonds (HBs) among the chains in all studied systems.

The specific heat measurements of powdered coin-shaped (10 mm in diameter, 2 mm thick) samples of 100 mg were carried out in a dilution refrigerator using a dual slope method [3] with a 6% inaccuracy. The magnetization was measured in a ^{4}He cryostat with a homemade vibrating sample magnetometer operating at 8.2 Hz with an inaccuracy better than 1.5%. Electron spin resonance (ESR) measurements of powdered samples were performed on a directsight radiospectrometer [4] in the frequency range 4-12 cm^{-1}.

2 Results and discussion

The magnetic field dependence of molar magnetic moment of all compounds measured at 4.27 K is in Fig.1. At this temperature no substantional differences in the magnetic properties of all powdered samples can be found. The systems resemble a behaviour of an S=1/2 paramagnet in magnetic field described by a Brillouin function with g-factors typical for octahedral copper(II) ion, i.e. 2.05 (I), 2.19 (II) and 2.13 (III). The perfect resembling of ideal paramagnet results from the crystal structure; the spins of unpaired electrons localized on Cu(II) ions are correlated via long exchange paths mediated by -N-C- Ni-C-N- units in (I) and -N-C-Ag-C-N- units in (II) and (III). Since for nickel(II) analogue of (I) the exchange path led to the intrachain exchange interaction $J/k_B \approx$ 0.2-0.6 K [5], the magnetization measurements suggest similar behaviour also for Cu(II) compounds. Specific heat studies performed in zero magnetic field revealed the substantional contribution of magnetic correlations in the milikelvin region. The Fig.2 represents the temperature dependence of specific heat of all compounds. Since only magnetic and phonon systems contribute to the specific heat and the latter may be safely neglected at temperatures of our interest, in further analysis the magnetic specific heat will be referred to the total specific heat. The specific heat of (I) and (II) which are characterized by the same local surrounding of Cu(II) ion is shown in Fig.2a. A significantly different behaviour of both studied systems is clearly indicated by a large difference in the amount of short-range order quantitatively estimated by magnetic entropy calculations; in the temperature range from 50 mK to 1 K, in (I) 80% of theoretical magnetic entropy $Rln(2S+1)$ for S=1/2 was removed above the phase transition while in (II) this amount was reduced to 30%. The same local surrounding of Cu(II) ion in both systems suggests very close values of exchange anisotropy resulting from the anisotropy of g-factors. It is confirmed by ESR measurements performed at 4.2 K yielding g_{par}=2.17±0.01, g_{per}=2.04±0.01 for (I) and g_{par}=2.19±0.01, g_{per}=2.03±0.01 for (II). The strength of the exchange anisotropy $\Delta J = J_{par} - J_{per}$ resulting from the anisotropy in g-factors is proportional to $\Delta g/g$ so other mechanism responsible for the observed discrepancies could be ascribed to the different exchange paths. The comparison of the specific heat of (II) and (III) (Fig.2b) does not support the assump-

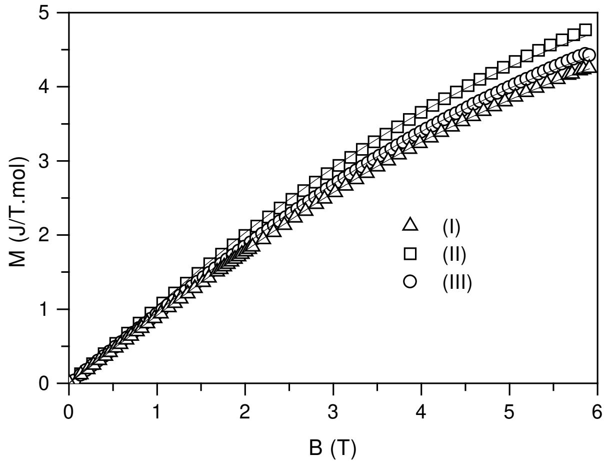

Fig.1. Magnetic field dependence of molar magnetic moment of (I) (△), (II) (□) and (III) (○). The solid lines represent Brillouin function with g-factors 2.05 (I), 2.19 (II) and 2.13 (III).

tion; since the estimation of g-anisotropy in (III) (g_{par}=2.25±0.01, g_{per}=2.07±0.01) is comparable with that of (II) it is obvious that the same exchange paths do not result in the same behaviour and the disproportion in the degree of short-range order observed in (II) (30%) and (III) (80%) still remains significant. Furthermore, the previous analysis of specific heat of (I) [5] performed in the frame of one-dimensional models revealed large deviations of the magnetic system from the chain-like behaviour (Fig.2a). These deviations were ascribed to the presence of additional exchange paths mediated by HBs which should be included to complete the net of exchange paths. This need arises from the fact that in the case of the elongated local octahedron the unpaired copper electron occupies $d_{x^2-y^2}$ orbital. Consequently, the -N-C-Ag/Ni- C-N- units do not represent the main exchange paths. This fact will stimulate more detailed structural studies with the aim to identify all possible HBs which could mediate exchange coupling. From this point of view, none of the studied compounds represents a good one-dimensional Heisenberg system due to large deviations from the chain-like behaviour. On the other hand, the extremely low values of exchange interaction ($\mid J \mid / k_B$ < 80 mK- 230 mK) previously estimated from the analysis performed within one-dimensional models together with the low values of transition temperatures T_c =130 mK (I), 80 mK (III) and T_c <40 mK (II) might indicate that at the lowest temperatures the magnetic properties of the title compounds will be governed by a combined effect of exchange and dipolar coupling. In the future, dipolar calculations are to be performed to estimate the role of both mechanisms in the formation of the ground state of studied systems [6].

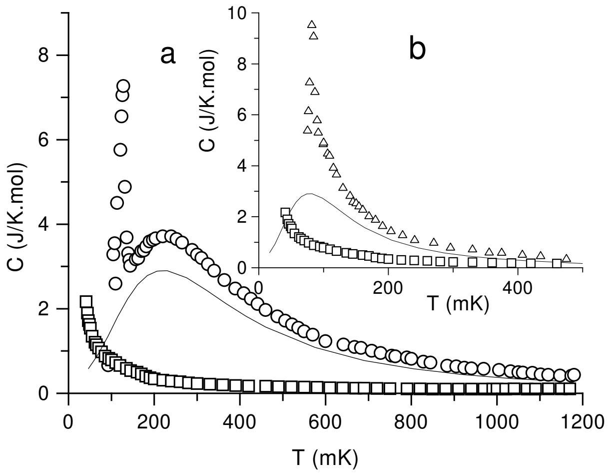

Fig.2a: Temperature dependence of specific heat of (I) (○) and (II) (□). The solid line represents S =1/2 antiferromagnetic Heisenberg chain with J/k_B =-230 mK.
Fig.2b: Temperature dependence of specific heat of (II) (□) and (III) (△). The solid line represents S =1/2 antiferromagnetic Heisenberg chain with J/k_B =-82 mK.

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References

[1] N. Papanicolaou, P. Spathis: *J. Phys. C: Solid State Phys.* **20** (1987) L783

[2] R.F. Wallis, D.J. Mills, A.D. Boardman: *Phys. Rev.* **B52** (1995) R3828 and references therein

[3] S. Riegel, G. Weber: *J. Phys. E: Sci Instrum.* **19** (1986) 790

[4] V.V. Eremenko, S.A. Zvyagin, V.V. Pishko, Yu.G. Pashkevich, V.V. Shakhov: *Sov. J. Low Temp. Phys.* **18** (1992) 175

[5] M. Orendáč, A. Orendáčová, J. Černák, A. Feher: *Sol. St. Comm.* **94** (1995) 833

[6] C.M. Wynn, M.A. Girtu, W.B. Brinckerhoff, K.I. Sugiura, Joel S. Miller: *Chem. Mater.* **9** (1997) 2156