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$CuBr_2(C_{10}H_8N_2)$ — $S = 1/2$ Two-Dimensional Rectangular Heisenberg Antiferromagnet

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Magnetic susceptibility and X-band electron spin resonance study of a two-dimensional Heisenberg antiferromagnetic system $CuBr_2$(bipy), where bipy = $C_{10}H_8N_2$ is 4,4′-bipyridyl, has been performed in the temperature range from 300 K down to 2 K. A rhombic anisotropy of the g-factor was obtained from X-band EPR measurements with $g_x = 2.037$, $g_y = 2.100$ and $g_z = 2.219$. The temperature dependence of the magnetic susceptibility with a round maximum observed at 28 K suggests antiferromagnetic type of short-range order. No signature of the magnetic long-range order in studied compound was observed. The comparison of the magnetic susceptibility data with a two-dimensional rectangular Heisenberg model yields the values of intralayer exchange couplings $J/k_B = -47$ K and $J'/k_B = -9.4$ K.

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1. Introduction

The two-dimensional quantum Heisenberg antiferromagnets (2D QHAF) with spin $S = 1/2$ have been extensively investigated mainly in connection with their relevance to the parent compounds of cuprate superconductors and important role of intralayer antiferromagnetic interactions in pairing mechanisms [1]. In the case of the ideal 2D QHAF on a square lattice, the magnetic long-range order is suppressed by zero-point fluctuations at any finite temperature [2]. Related magnetic systems as rectangular HAF system (formed by chains with intrachain interaction J and interchain J', $0 \leq J'/J \leq 1$) described by the Hamiltonian

$$H = -J \sum_{i=1}^{n} \sum_{j=1}^{n} \left(S_{i,j} S_{i+1,j} + \alpha S_{i,j} S_{i,j+1} \right), \qquad (1)$$

where $\alpha = J'/J$, represents the model system to investigate the crossover from 2D HAF with the Néel ordered ground state to one-dimensional spin-chain system with disordered ground state [3].

This work is devoted to the study of magnetic properties of a material from the class of CuX_2(bipy), where bipy = $C_{10}H_8N_2$ is 4,4′-bipyridyl and X = Cl, Br [4, 5], which belong to prototypical $S = 1/2$ rectangular HAF systems. The material $CuBr_2$(bipy) crystallizes in a monoclinic lattice (space group $C2/m$) and represents structurally a system with rectangular covalent layers formed in bc plane. Octahedral coordination of $S = 1/2$ Cu(II) ions is formed by four bromine ions and two nitrogen ions with a rhombic distortion due to the Jahn–Teller effect with two Cu–Br (3.195 Å) bonds longer than the other two Cu–Br (2.442 Å) and two Cu–N (2.075 Å) bonds [4].

2. Experimental

The electron spin resonance (ESR) experiment was performed in a home-made X-band ESR spectrometer with a low-temperature cavity resonator, where the absorption signal is measured directly. 2,2-diphenyl-1--picrylhydrazyl (DPPH) was used as a g-marker. The magnetic susceptibility was studied in the temperature range from 2 K to 300 K using a commercial SQUID magnetometer. The background signal from the gelatin capsule and diamagnetic contribution of the sample, $\chi_{DIA} = -1.987 \times 10^{-9}$ m^3 mol^{-1}, estimated from the Pascal constants [6] were subtracted from the raw susceptibility data. The ESR and magnetic measurements were carried out on powdered samples.

3. Results and discussion

The ESR spectrum obtained at 4.2 K and 10.27 GHz with asymmetric shape typical for a number of randomly oriented crystallites with rhombic symmetry of g--tensor was analyzed using ESR spectra simulation package EasySpin [7]. The best fit to the experimental data using a least-squares method (Fig. 1) was obtained for $g_x = 2.037$, $g_y = 2.100$ and $g_z = 2.219$ and the halfwidth of the resonance line $\Delta B = 7.2$ mT. The observed rhombic anisotropy of the g-tensor is typical for a structural distortion of the coordination octahedron as shown by structural data. It is characterized by the presence of an unpaired electron in $d_{x^2-y^2}$ orbital, which has lobes oriented along Cu–N bonds and two shorter Cu–Br bonds. The exchange paths create magnetic rectangular lattice in the bc plane, however, exchange coupling is expected to be weaker along the b axis with significantly longer superexchange pathway (Cu–bipy–Cu) than that along the c axis (Cu–Br_2–Cu).

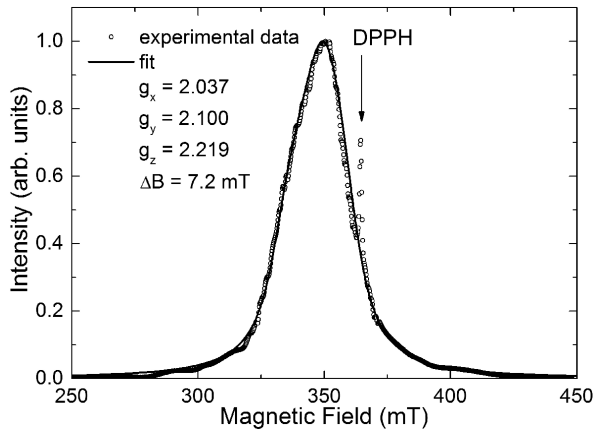

Fig. 1. Powder ESR spectrum of $CuBr_2$(bipy) measured at 4.2 K and 10.27 GHz (circles). The solid line represents the best fit to the experimental data using ESR spectra simulation package EasySpin [7] with $g_x = 2.037$, $g_x = 2.100$ and $g_x = 2.219$ and the halfwidth of the resonance line $\Delta B = 7.2$ mT.

The temperature dependence of the magnetic susceptibility of $CuBr_2$(bipy) measured at 100 mT (Fig. 2) is characterized by the presence of a round maximum at 28 K and a Curie-like tail at the lowest temperatures, which is usually attributed to the intrinsic magnetic impurities (edge spins, fragments) in powdered samples. No difference between the magnetic response of the field--cooled and zero-field-cooled sample was observed indicating that no transition to the long-range ordered state occurs down to 2 K in $CuBr_2$(bipy). Using the Curie–Weiss model to fit the magnetic susceptibility data in the region 100–300 K yields the Curie temperature $\Theta = -43$ K and $g = 2.13$.

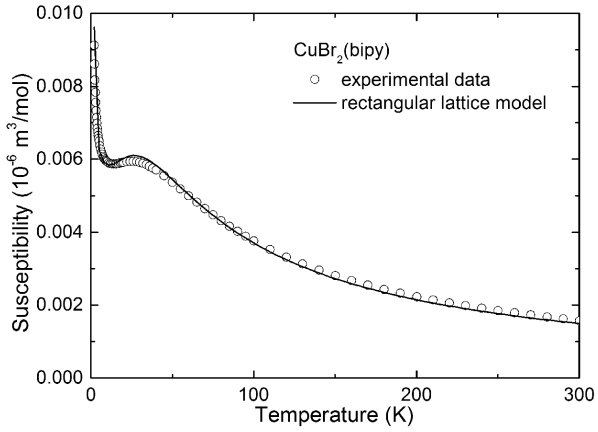

Fig. 2. Magnetic susceptibility of $CuBr_2$(bipy) measured at 100 mT. The solid line represents the fit of the rectangular lattice model [8] to the experimental data (circles), including the contribution of intrinsic paramagnetic impurities to the low temperature tail. The best agreement was obtained for the ratio $\alpha = 0.2$ with $J/k_B = -47$ K and $g = 2.04$.

Since there is no analytical expression available in literature for the susceptibility of a rectangular lattice, equations derived from the Monte Carlo simulations of the system described by Eq. (1) by Butcher et al. [8] were adopted to analyze the experimental data. The comparison of our data to the Monte Carlo simulations suggested the ratio $\alpha = 0.2$ as appropriate for the description of magnetic susceptibility of $CuBr_2$(bipy). The best agreement of this model with the experimental data, including the contribution of 2.5% of intrinsic paramagnetic impurities described by Curie law, was obtained for $J/k_B = -47$ K (yielding $J'/k_B = -9.4$ K for $\alpha = 0.2$) and $g = 2.04$ as shown in Fig. 2. This result suggests the presence of a spatially anisotropic exchange coupling in $CuBr_2$(bipy) as expected from the crystal structure and local electronic configuration of Cu(II) ions.

4. Conclusion

In conclusion, we performed spectroscopic and magnetic studies of 2D HAF $CuBr_2$(bipy). The analysis of experimental data reveals the presence of 2D spatially anisotropic (rectangular) magnetic lattice with the ratio of intralayer exchange couplings $\alpha = J'/J = 0.2$ and strong dominant exchange coupling $J/k_B = -47$ K along Cu–Br_2–Cu superexchange pathway. The influence of the interlayer exchange coupling on the presence of a long--range order at very low temperatures is the subject of further specific heat studies in the millikelvin temperature range.

Acknowledgments

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