

Study of low-dimensional magnetism in zeolitic imidazolate frameworks

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Zeolitic imidazolate frameworks (ZIFs) are a class of porous metal-organic frameworks composed of tetrahedrally-coordinated transition metal ions connected via imidazolate linkers. This work is devoted to the study of $[\{Zn(mIm)_2 \cdot 2H_2O\}_\infty]$ known as ZIF-8 and $[\{Cu(mIm)_2 \cdot 2H_2O\}_\infty]$, abbreviated as Cu-ZIF-8 (HmIm = 2-methylimidazole). Cu-ZIF-8 can be considered as a structural analog of ZIF-8, since it was found that partial replacement of the Zn(II) ion for Cu(II) did not modify the crystal structure. The heat capacity of powdered samples was measured from 0.4 to 300 K in magnetic fields up to 9 T. Both ZIF-8 and Cu-ZIF-8 data sets are nearly identical, suggesting that the lattice dynamics is not sensitive to the Cu-Zn substitution. At low temperatures, in $B = 0$ the heat capacity of the nonmagnetic ZIF-8 drops to zero, while the Cu-ZIF-8 data form a round maximum at about 0.4 K. The application of nonzero fields leads to the significant reduction of the maximum and its shift towards higher temperatures. The temperature dependence of the magnetic susceptibility of polycrystalline samples was measured in constant magnetic fields of 10 mT and 1 T at temperatures from 2 to 300 K in field cooling (FC) and zero field cooling (ZFC) regimes. The ZFC susceptibilities of Cu-ZIF-8 and ZIF-8 are characterized by a sharp maximum at about 50 K which shifts towards lower temperatures in the FC data. The origin of the sharp maximum is most likely related to the atmospheric oxygen present in the pores of our compounds. At higher temperatures, FC and ZFC data of Cu-ZIF-8 are identical and are characterized by a broad maximum at about 130 K which can be described within the model of Heisenberg antiferromagnetic chain with spin 1/2, intrachain coupling $J/k_B \sim 217K$ and $g=2$. Such strong coupling preserved observation of the corresponding magnetic contribution with the maximal value $C_{max} \sim 3J/Kmol$ at about 100 K in the experimental specific heat which is dominated by lattice contribution. The origin of the low-temperature magnetic specific heat is discussed.

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