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Formation of the $S = 1$ paramagnetic centers in the bond-diluted spin-gap magnet $(\text{C}_4\text{H}_{12}\text{N}_2)(\text{Cu}_2\text{Cl}_6)$

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Abstract. Recently found quasi-two dimensional metalloorganic compound $(\text{C}_4\text{H}_{12}\text{N}_2)(\text{Cu}_2\text{Cl}_6)$ (abbreviated PHCC) is an example of a spin-gap magnet. Its ground state is a nonmagnetic singlet separated from the triplet excitations by an energy gap of approximately 1 meV. This compound allows partial substitution of chlorine ions by bromine, which results in the modulation of the affected exchange bonds. We have found by means of electron spin resonance spectroscopy that this doping results in the formation of the gapless $S = 1$ paramagnetic centers. These centers can be interpreted as triplet excitations trapped in a potential well created by doping.

1. Introduction

Spin-gap magnets are one of the focus topics of modern magnetism [1]. Due to a particular architecture of the exchange bonds, which frequently invokes dimer motives, these magnets remains in the disordered singlet ground state to the lowest temperatures despite strong antiferromagnetic interspin interaction. The stability of the singlet ground state versus conventional forms of (antiferro)magnetic order is granted by the energy gap of exchange origin separating singlet ground state from the excited triplet excitations. Quasi-two dimensional spin-gap magnet $(\text{C}_4\text{H}_{12}\text{N}_2)(\text{Cu}_2\text{Cl}_6)$ (also called PHCC, or piperazinium hexachlordicuprate) is one of the test compounds of this sort [2].

The magnetic subsystem of PHCC can be envisioned as layers of strongly coupled dimers, the inelastic neutron scattering experiments suggest that 6 to 8 relevant exchange bonds are present [2, 3]. All these exchange couplings are indirect superexchange pathes mediated by halogen ions. Thus, partial substitution of chlorine by bromine does not deplete magnetic subsystem of PHCC but, instead, modifies exchange bonds mediated by the substituted ion. The samples of $(\text{C}_4\text{H}_{12}\text{N}_2)(\text{Cu}_2\text{Cl}_6(1-y)\text{Br}_y)$ with nominal bromine content $x$ up to 12% can be grown. We will use nominal concentration for the sample identification as was used in previous works. Detailed structural analysis [4] shows that the actual bromine occupancy is linear with nominal one but slightly differs for different inequivalent positions, the bromine substituted PHCC has the same

Electron spin resonance (ESR) is a sensitive technique to study low energy dynamics of magnetic systems. It allows to study fine details of the excitations spectrum with the routine resolution of less then 1 GHz (which corresponds to the energy of 5µeV) thus complementing powerful inelastic neutron scattering method. Since the ESR absorption spectra is recorded as a field scan, it becomes possible to separate contributions of different magnetic systems which is impossible to extract from the bulk magnetization measurements. Intensity of the ESR absorption is directly proportional to the static susceptibility and to the amount of spins. The shape of ESR absorption spectrum allows to definitively distinguish paramagnetic centers with different spin.

In the present report we will briefly discuss ESR of triplet excitations and impurity-induced multispin defects in pure and bromine-substituted PHCC. We will demonstrate that fine structure of the energy spectrum of collective excitations of the spin-gap magnet can be accessed by means of ESR and that bond-doping results in the formation of unusual multispin objects.

2. ESR of collective triplet excitations in the nominally pure sample

ESR on nominally pure PHCC was described in details in [6]. Representative absorption spectra are shown in figure 1. As expected for a spin-gap system, at temperatures below the energy scale of the gap in the excitation spectrum (in the case of PHCC the gap $\Delta = 1.02\text{meV}$ or 12 K) the population of magnetic excitations decreases and the ESR absorption loses intensity.

On cooling below approximately 4K ESR absorption line splits in several subcomponents, which can be identified as a multicomponent signal from the triplet excitations (components "A", "B" and "C" in figure 1) and a signal from the residual paramagnetic defects (denoted "PM" in figure 1). Absorption from the triplet excitations continues to decrease on cooling and vanishes below 2K, while the signal from residual defects follows Curie law. The amount of residual paramagnetic centers was estimated from static magnetization measurements as less than 0.04% per copper ion.

The multicomponent absorption signal of triplet excitations is, in fact, a typical absorption spectrum of the $S = 1$ spin in an effective crystal field — it is due to the fine structure of the excitation spectrum because of anisotropic spin-spin interactions. The effective crystal field affecting triplet excitations can be described by anisotropic contribution to the triplet excitations' Hamiltonian:

$$H_{\text{anis}} = D S_z^2 + E(S_x^2 - S_y^2)$$

here $x, y, z$ is a cartesian basis for anisotropic Hamiltonian, which is not directly related to the crystallographic frame of reference because of low (triclinic) symmetry of the crystal.

Joint analysis of the angular dependencies of split ESR absorption at $T=3K$ [6] allowed to determine the magnitude of anisotropy constants $D = (-7.90 \pm 0.28)\text{GHz} (-33\text{µeV})$ and $E = (-1.34 \pm 0.19)\text{GHz} (-5.6\text{µeV})$ as well as orientation of anisotropy axes with respect to the crystallographic frame of reference. This means that the energies of the triplet sublevels at zero field are $\Delta$ and $\Delta + D \pm E$, here the gap $\Delta = 1.02\text{meV}$.

3. Low-temperature ESR of multispin paramagnetic centers in the bond-diluted PHCC

Investigation of the ESR in bond-diluted PHCC was reported in details in [7, 8]. Examples of ESR absorption spectra in the nominally 10% doped sample are shown in figure.1. The main difference from the pure sample is that the ESR absorption is observed at low temperatures down to 450 mK. This low-temperature ESR signal again can be separated into some sort of
irregularly shaped signal with $g \approx 2$ which is most likely due to some paramagnetic defects and three-subcomponents absorption which is typical for the $S = 1$ objects.

This low-temperature signal from $S = 1$ objects differs from that of triplet excitations in pure PHCC in certain ways. First, its temperature evolution indicates absence of the energy gap (or, at least, the gap is below 400 mK or 50 $\mu$eV). Second, one can see that at low temperatures left component "B" dominates, while for the pure sample at 2.5—4 K right component "C" was more intense. Finally, splitting between "B" and "C" components is slightly different in comparison with pure PHCC. This means that the low-temperature absorption observed in doped samples is not due to delocalized triplet excitations. Note also that these $S = 1$ centers are formed under nonmagnetic bond-dilution in the system of strongly coupled $S = 1/2$ spins which has a non-magnetic (singlet) ground state.

Intensity of the ESR absorption can be scaled to static susceptibility measured on the same samples above 2K which allows to derive the amount of these new objects from the ESR data.
(figure 2). We have found [7] that the concentration of $S = 1$ centers is $(0.4 \pm 0.1)\%$ per molecule of PHCC for the nominally 10% doped sample. As the building block of PHCC structure is a Cu$_2$Cl$_6$ dimer, we can conjecture that the $S = 1$ center is formed around the dimer with two bridging chlorines substituted by bromine. Structural refinement of Ref. [4] shows that actual bromine occupancy of interdimer halogen positions for the nominally 10% bromine-diluted sample is 7.5%, which yields probability of the double substitution about 0.56%.

To check this conjecture we have performed similar experiments for the samples with nominal bromine content of 5 and 7.5%: high-temperature (above 5K) absorption was scaled to the known static susceptibility which allowed to set the same scale to the absorption spectra measured on different samples (see figure.2). We observe increase of the $S = 1$ objects response with increasing concentration which is in agreement with $I \propto x^2$ dependence which follows from our "double

Figure 2. (a) Imaginary part of the high-frequency magnetic susceptibility $\chi''$ at 0.45K for the samples with different bromine content scaled to the same units. Absorption components due to the formed $S = 1$ objects are marked as "A" and "B", absorption component due to the uncontrolled defect is marked as "PM". Solid lines for $x \neq 0$ shows lorentzian fits of the "B" component used for intensity analysis on panel (b). (b) Concentration dependency of the "B" component intensity for the bromine-substituted PHCC at 0.45K. (c) Temperature dependency of the intensity of ESR absorption components for the 10% nominally bromine diluted sample. Solid lines — fits in the model of gapless $S = 1$ objects (see Ref.[7] for details).
substitution” conjecture. Note also that intensities of ”PM” component in bromine-diluted samples do not strongly exceed that of pure sample, which is known to correspond to 0.04% of $S = 1/2$ defects per copper ion [6]. Thus, no additional paramagnetic centers in the amount comparable to the bromine concentration is formed.

The extreme scenario of formation of such a gapless $S = 1$ center is that the interdimer coupling turns ferromagnetic on double substitution. This is not utterly impossible as the bond angles there are close to 90° and as it is known that interdimer coupling in PHCC is the most susceptible to the hydrostatic pressure [9]. However, this effect can be re-interpreted in other way, which does not require extreme variation of coupling. Namely, bond doping changes local coupling constants, which is equivalent to formation of some potential relief for the propagating triplet excitations. If this potential happens to be attractive, then the potential well for the triplet excitation is formed. As the PHCC is two-dimensional magnet and 2D potential well always have a bound state, it can be possible that a low-lying bound state trapping one of the triplet excitations can be formed even without actual formation of ferromagnetic bond. The resulting $S = 1$ low-energy object is then a multispin defect spread in the certain vicinity of the attracting center.

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