Magnetic resonance of collective states in spin-gap magnets

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Abstract

Various types of magnetic resonance signals observed in quantum-disordered magnets of the Haldane and dimer types are reported. The collective states of correlated spins near the breaks of the $S = 1$ spin chains in the Haldane magnet $PbNi_2V_2O_8$ demonstrate magnetic response of an effective spin $S = 1/2$, while the excited states of long chains reveal the ESR spectrum of an effective spin $S = 1$ in a crystal field. A magnetic resonance spectrum of the latter type is also observed for the collective excited states in the system of coupled $S = \frac{1}{2}$ dimers in crystals of $TlCuCl_3$. Further, the interaction of triplet excitations and defects in $PbNi_2V_2O_8$ is shown to result in a hybrid spin resonance mode.
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1. Introduction

Spin-gap magnets attract much interest because of the quantum disordered and strongly correlated ground states and because of unusual magnetic properties with magnetic susceptibility vanishing at low temperatures. The gap in the spectrum of spin excitations, separating a singlet ground state from the magnetic states, is known to be present in the spin $S = 1$ spin chains (Haldane magnets [1]) in dimerised $S = \frac{1}{2}$ spin chains (alternated spin chains and spin-Peierls magnets [2]), dimer spin systems [3], etc. The energy gap in the spectrum of magnetic excitations provides a low temperature interval where the quantized excitations may be considered as a rare gas of quasiparticles. These excitations are triplets carrying spin $S = 1$ and their spin sublevels are split by the crystal field. Thus, they should give magnetic resonance signals analogous to the signal of separated spins $S = 1$ in a crystal field, despite the concentrated magnetic system with strong exchange interaction [4]. Therefore, we expect magnetic resonance signals with the single-ion features but originating from the collective states of exchange coupled ions. Here, we review

and compare magnetic resonance spectra of triplet excitations in the Haldane magnet $PbNi_2V_2O_8$ and in the dimer spin-gap magnet $TlCuCl_3$, as well as other related magnetic resonance signals which may be observed due to the quantum nature of the spin-gap magnetic structures. Some of the described results were reported in Refs. [5–7].

2. Effective spins at the end of spin chains in the Haldane magnet

A sophisticated example of the collective spin states in a quantum magnet is the spin structure formed near the ends of the spin $S = 1$ chains in a Haldane magnet. Breaks of the spin chains arise at the doping by nonmagnetic impurities, inserted instead of a small amount of magnetic $S = 1$ ions. The nonzero spin projections are restored near the chain ends and thus, areas of the local antiferromagnetic order appear near impurity atoms. The spin structure at the chain end was calculated by Monte-Carlo simulation in Ref. [8]: the magnetic ions at the edges of the spin chain have maximal spin projections, and the absolute value of the correlated spin projections decays exponentially away from the chain end according to the correlation length $\xi \simeq 7a$, here a is the interspin distance. The total spin of such a correlated area appears to be $S_{eff} = \frac{1}{2}$ in accordance

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with the resonant valence bonds consideration [9]. Electron spin resonance is a convenient tool to measure the effective spins of microscopic objects in crystals, because for $S \geqslant 1$ the spin sublevels are split by the crystal field and for $S_{eff} = \frac{1}{2}$ there is no splitting. The first experimental evidence for $S_{eff} = \frac{1}{2}$ at the ends of Haldane chains was obtained in observations of the ESR of the Haldane magnet $[Ni(C_2H_8N_2)_2(NO_2)]ClO_4$ (abbreviated as NENP) at the substitution of a small amount of Ni^{2+} ions by magnetic ($S = 1/2$) Cu^{2+} ions [9]. The resulting spectra were interpreted using a model of three coupled spins: two effective spins at the ends of spin chains and a Cu-ion spin between them. The inorganic Haldane magnet $PbNi_2V_2O_8$ has an advantage of high solubility for different non-magnetic impurities, allowing one to find magnetic degrees of freedom elaborated by doping and to study the concentration dependencies. We observed a resonance absorption with a Curie-like intensity and without any crystal-field splitting for different impurity concentrations in ceramic samples of $PbNi_2V_2O_8$ doped with nonmagnetic Mg. The absence of the crystal field splitting comparable to the single ion anisotropy constant 56 GHz (measured in Ref. [10]) resolves spin $S = \frac{1}{2}$ degrees of freedom provided by doping. The resonant absorption lines are presented in Fig. 1, and the corresponding frequency-field dependence at the Fig. 2.

Comparison of the ESR lines recorded for the samples with the different concentration of nonmagnetic impurities (see Fig. 1) shows a sufficient increase of the linewidth when the concentration is enlarged from 0.01 to 0.02. The increase in linewidth indicates a strong interaction between the areas of the local antiferromagnetic order when the average length of spin chain fragments is $50a$. Taking into account that most of the chain fragments are shorter than the average length, we get the estimation of the length of
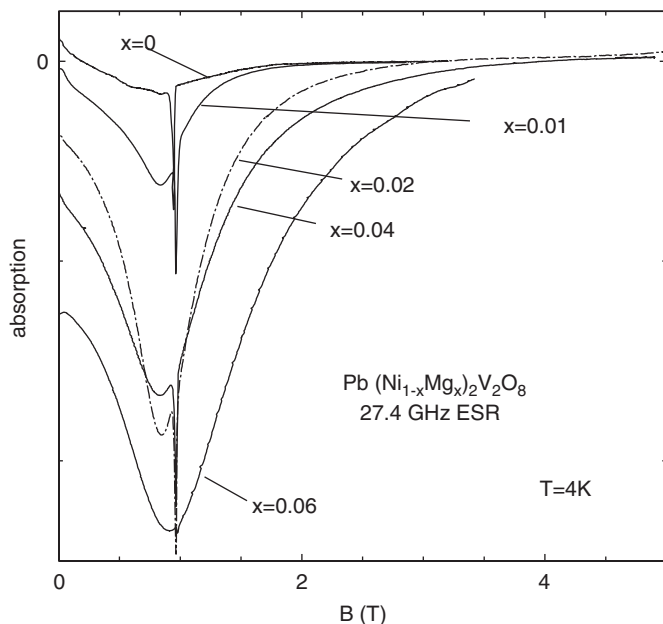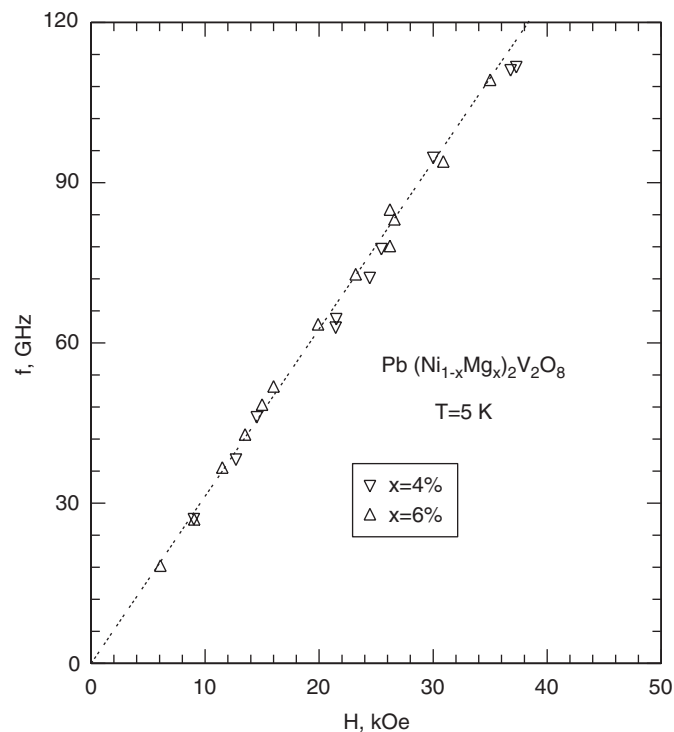

Fig. 2. Frequency-field diagram for the magnetic defects created in the Haldane magnet $PbNi_2V_2O_8$ by nonmagnetic doping.

the correlated area with nonzero spin projections of the order of $10a$, which corresponds to the theoretical correlation length of $7a$.

3. ESR of the triplet excitations in the Haldane magnet

Magnetic excitations in spin-gap magnets may be thermally activated by heating the sample to the temperature comparable with the spin gap, which is approximately 40 K for the Haldane magnet $PbNi_2V_2O_8$. As mentioned above, at low temperatures, the excitations may be considered as a rare gas of noniteracting quasiparticles. Thus, a single-ion like signal should appear at heating as the population number of excitations increase. Indeed, a thermally activated absorption was observed in ceramic samples of $PbNi_2V_2O_8$, as illustrated in Fig. 3. The thermally activated absorption is well separated from the signal of residual defects, which is located near the position, corresponding to the g-factor of free spins equal to 2.0. The thermally activated absorption at low frequencies is observed at the fields far above the paramagnetic resonance field, while for frequencies of about 100 GHz it is located near zero field. These resonance fields measured for several frequencies correspond well to the spectrum of the isolated $S = 1$ ions in a polycrystal with the single-ion uniaxial anisotropy constant $D_{eff} \simeq 86$ GHz. Absorption in zero field should arise on the frequency near the D_{eff}-value, and at the low frequency limit, the most intensive absorption in the powder sample should be at the magnetic field of $D_{eff}/g\mu_B$.

Fig. 1. ESR lines at various Mg-concentration in $PbNi_2V_2O_8$, $T = 4$ K.