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Electron spin resonance investigation of the spin-1/2 kagomé antiferromagnet $ZnCu_3(OH)_6Cl_2$

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Abstract. We report a temperature and frequency dependent electron spin resonance (ESR) study of the kagomé spin-1/2 compound $ZnCu_3(OH)_6Cl_2$. Our results demonstrate that two spin species are simultaneously detected; copper spins on the intra-plane Cu^{2+} kagomé sites and those on the inter-plane Zn^{2+} sites, the latter resulting from the Cu^{2+}/Zn^{2+} antisite disorder. We examine all the possible magnetic anisotropy terms, which could lead to the observed extremely broad ESR lines in this system. We argue that the line broadening is due to Dzyaloshinsky-Moriya interaction.

1. Introduction

For the last two decades the spin-1/2 kagomé antiferromagnet, a 2D network of corner-sharing triangles, has been at the forefront of the pursuit of novel quantum phenomena [1], in relation to geometrical frustration, which prevents from simultaneous energy minimization of all the bonds. Despite intensive studies, a clear understanding of its ground state still remains a major challenge. This can be partially attributed to a lack of model compounds, which would allow unambiguous experimental tests of theoretical predictions.

Quite recently, the Cu^{2+}-based $ZnCu_3(OH)_6Cl_2$ has been proposed as the first "structurally perfect" spin-1/2 kagomé lattice [2], showing no sign of magnetic instabilities down to the lowest accessible temperatures [3, 4, 5]. However, it was later established that even the purest compounds possess significant Cu^{2+}/Zn^{2+} antisite disorder, resulting in 4-7% of the copper ions occupying the inter-layer Zn^{2+} sites [6, 7, 8]. It was also suggested that magnetic anisotropy in the form of a Dzyaloshinsky Moriya (DM) interaction [9] could be important in this compound [7, 10, 11]. Here, we report an electron spin resonance (ESR) investigation, which is particularly powerfull for addressing all questions related to magnetic anisotropy. It allows us to quantify the DM interaction in $ZnCu_3(OH)_6Cl_2$. Part of our results were initially published in Ref. [12].

2. Experimental results

We have performed an extensive ESR investigation on a polycrystalline $ZnCu_3(OH)_6Cl_2$ sample, synthesized as described in Ref. [2]. The measurements were performed between room-

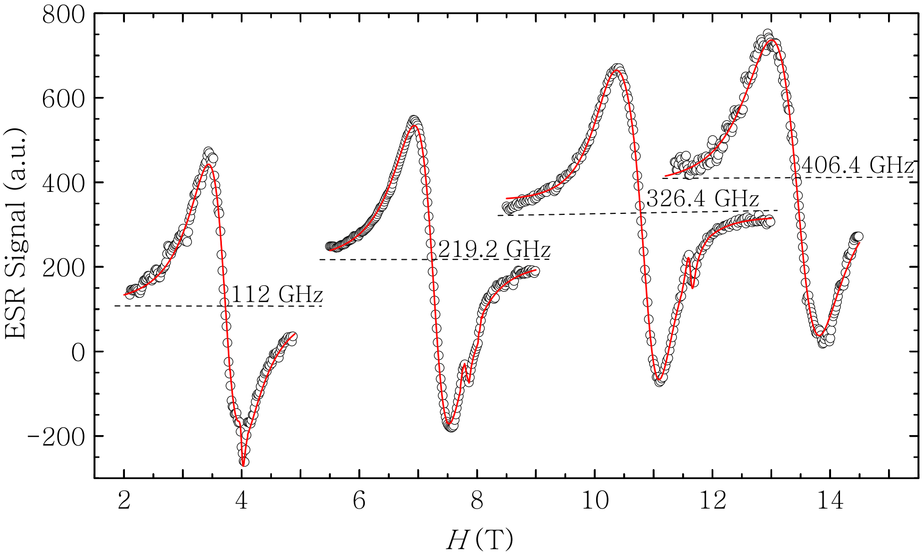

Figure 1. RT ESR spectra (○) of $ZnCu_3(OH)_6Cl_2$, vertically translated for clarity, with the base lines (- - - -) displaying the frequency of acquisition, and the corresponding fits (——).

temperature (RT) and 5 K in the frequency range between ∼100 GHz and ∼400 GHz. In Fig. 1 we show typical RT derivative ESR spectra, recorded at different frequencies. The spectra consist of two components – a dominant broad one and a narrower one shifted to higher fields.

In Fig. 2(a) the linear scaling of the resonance field with frequency, characteristic for the paramagnetic response, is shown for the two components. It yields the RT g-factor value $g_n = 2.00$ for the narrow component and the average g-factor value $\bar{g} = 2.18$ for the broad one. We can ascribe the narrow component of the spectra to a minority impurity phase, since its intensity represents only 0.2% of the total ESR intensity and its g-factor is close to the free-electron value. In order to fit the ESR lineshape, g-factor anisotropy $g(\theta) = (g_{\|}^2 \cos^2(\theta - \theta_g) + g_{\perp}^2 \sin^2(\theta - \theta_g))^{1/2}$ has to be introduced for the broad component. Here θ represents the angle between an applied magnetic field H and the normal c to kagomé planes while $\theta_g = \pi/5$ stands for the tilt of CuO_4 plaquettes with respect to the kagomé planes [2], locally setting the orientation of principal g-factor axes. The resulting powder field distribution is convoluted with a Lorentzian having angular dependent line-width $\Delta H(\theta) = (\Delta H_z^2 \cos^2\theta + \Delta H_p^2 \sin^2\theta)^{1/2}$, where ΔH_z and ΔH_p correspond to the direction parallel and perpendicular to c. A second Lorentzian is added to account for the narrow component. The corresponding fits at RT (Fig. 1) yield principal g-factor values $g_{\|} = 2.25$, $g_{\perp} = 2.14$ and line-width anisotropy $\Delta H_z = 1.19(4)$ T, $\Delta H_p = 0.95(3)$ T for the broad component at RT, with no significant frequency dependence [Fig. 2(b)].

The absolute value of the integrated ESR intensity at RT can be estimated by comparing it to a reference sample (0.08% diluted BDPA in polystyrene) with a known spin concentration of paramagnetic centers. The obtained ESR susceptibility $\chi_{ESR} = 1.0(2)$ emu/molCu is in agreement with the bulk susceptibility $\chi_b = 1.1$ emu/molCu. This reveals that ESR effectively detects all the Cu^{2+} magnetic moments in $ZnCu_3(OH)_6Cl_2$. The measured ESR response is thus intrinsic to the investigated compound.

In Fig. 3(a) we demonstrate that χ_{ESR} behaves similarly to χ_b down to 5 K. This is in clear contrast to the kagomé-planes susceptibility revealed by ^{17}O NMR [7], which decreases at lower temperatures. This experimental finding indicates that ESR is simultaneously detecting both

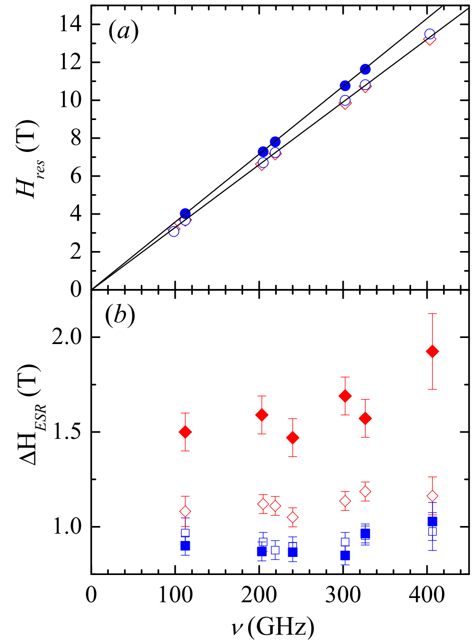

Figure 2. (a) Resonance field of the broad ESR line (○ ,◇) and the impurity line (●), at 280 K (○ ,●) and at 5 K (◇). (b) Frequency dependence of ΔH_z (◇) and ΔH_p (□) at RT (open) and 100 K (full).

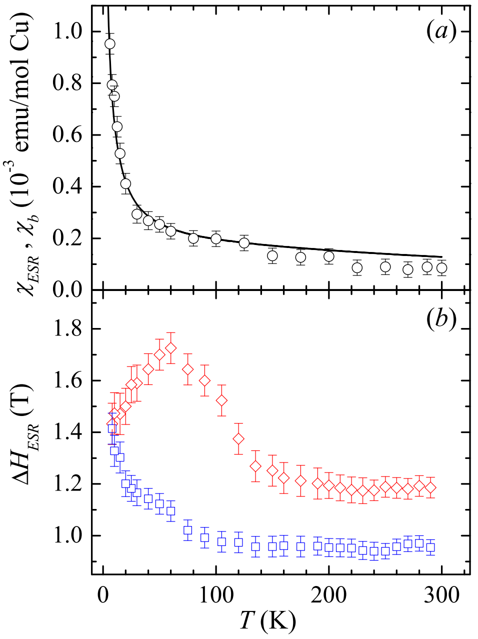

Figure 3. (a) Scaling of the ESR intensity χ_{ESR} (○) with bulk susceptibility χ_b (——). (b) Temperature dependence of the out-of-plane ΔH_z (◇) and the in-plane ΔH_p (□) ESR line-width.

the Cu^{2+} moments on the kagomé-planes and the inter-plane Cu^{2+} moments on Zn^{2+} sites, the latter being due to the Cu^{2+}/Zn^{2+} disorder. The fact that we find a *single* ESR line can then be understood in the context of a rather significant exchange coupling J' between the two species. Namely, the two species will yield a single exchange-narrowed ESR line when this coupling is above their Zeeman energy difference, $J' > \delta g \mu_B H \sim 1$ K. In addition, the T-dependence of the line-width speaks in favor of a multi-species ESR response. In the case of a single species the increase of ΔH_z below ∼150 K, which indicates the development of spin correlations below that temperature, would be expected to be monotonous with decreasing temperature. On the contrary, it shows a marked maximum around ∼50 K. In the context of the inter-site mixing, this implies that the ESR signal, although predominantly influenced by the majority Cu^{2+} moments on the kagome sites at higher temperature, at low temperatures is dominated by the inter-layer Cu^{2+}. Such scenario is endorsed by ESR measurements on different compositions $Zn_xCu_{4-x}(OH)_6Cl_2$ [12], however a quantitative explanation is still missing. We note that the increase of the line-width is anisotropic, indicating an anisotropic growth of spin correlations.

3. Discussion

We wish to stress that the ESR spectra of $ZnCu_3(OH)_6Cl_2$ are extremely broad. Since the ESR line-width is directly related to the magnetic anisotropy present in the spin Hamiltonian, this provides evidence of a sizable magnetic anisotropy term A in $ZnCu_3(OH)_6Cl_2$. As expected, the spectra have a Lorentzian shape due to fast electronic fluctuations induced in the paramagnetic regime by strong isotropic exchange $J = 190$ K [4]. In this case, the ESR line-width is estimated as $\Delta H \sim A^2/J$ [13], yielding $A \sim 16$ K.

In spin-1/2 systems, the ESR line-broadening is either an evidence of crystal field effects, resulting in the g-factor anisotropy and/or anisotropic exchange, due to dipole-dipole interactions between the electron spins or due to a hyperfine coupling with nuclear spins [14]. In $\mathrm{ZnCu_3(OH)_6Cl_2}$ the dipolar fields are of the order of 0.1 T and the hyperfine coupling is 0.02 T for $\mathrm{Cu^{2+}}$ ions [14]. These two mechanisms would therefore yield line-widths of only few Gauss. Next, the g-factor anisotropy is already incorporated in our fits, so that it doesn't contribute to the broad line-widths [Fig. 2(b) and Fig. 3(b)]. We also discard the possibility of the $\mathrm{Cu^{2+}/Zn^{2+}}$ antisite disorder as an important source of line-broadening. The line-width does not depend on the composition in $\mathrm{Zn}_x\mathrm{Cu}_{4-x}\mathrm{(OH)_6Cl_2}$ at least down to $x = 0.5$ [12], implying that the influence of the inter-layer $\mathrm{Cu^{2+}}$ spins on the ESR spectra at RT is marginal. Also a distribution of g-factors due to local distortions caused by the $\mathrm{Cu^{2+}/Zn^{2+}}$ disorder, which could potentially lead to g-strain broadening effects, can be ruled out as a possible broadening mechanism. Namely, in such case, the line-width would exhibit pronounced frequency dependence [14], while in $\mathrm{ZnCu_3(OH)_6Cl_2}$ it is frequency independent at RT [Fig. 2(b)]. There seems to be a slight frequency dependence of ΔH_z at 100 K, which can probably be attributed development of the spin correlations below ~150 K, which might be different in different frequency windows.

The observed broad ESR lines can thus only be assigned to significant exchange anisotropy, resulting from a spin-orbit coupling. The antisymmetric DM interaction $\mathbf{D}_{ij}\cdot\mathbf{S}_i \times \mathbf{S}_j$ is a result of the first order perturbation calculation, while the second order leads to a symmetric anisotropic exchange. When allowed by symmetry [9] the DM interaction is regularly the dominant magnetic anisotropy. In $\mathrm{ZnCu_3(OH)_6Cl_2}$, two components of the DM vector are allowed; the out-of plane D_z and the in-plane D_p, forming a DM pattern determined by the symmetry of the lattice [12]. The line-width anisotropy at RT can be well accounted for by assuming $|D_z| = 15(1)$ K and $|D_p| = 2(5)$ K [12]. The DM magnetic anisotropy is thus sizable ($D/J \approx 0.08$) and might crucialy affect the low-T properties of $\mathrm{ZnCu_3(OH)_6Cl_2}$ [15].

4. Conclusions

We have presented ESR results of the 2D kagomé compound $\mathrm{ZnCu_3(OH)_6Cl_2}$. The width of the spectra yields an appreciable magnetic anisotropy term. We argue that this has to be ascribed to the Dzyaloshinsky-Moriya interaction, $D/J \approx 0.08$. Implications of such a significant anisotropy on the magnetic ground state and low-lying excitations of the spin-1/2 kagomé antiferromagnet should prove to be important, possibly yielding complex quantum phenomena.

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