A new collective phenomenon arising from spin anisotropic perturbations to a Heisenberg square lattice manifested in paramagnetic resonance experiments

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We report unexpected behaviour in a family of Cu spin-\(\frac{1}{2}\) systems, in which an apparent gap in the low energy magneto-optical absorption spectrum opens at low temperature. This previously-unreported collective phenomenon arises at temperatures where the energy of the dominant exchange interaction exceeds the thermal energy. Simulations of the observed shifts in electron paramagnetic resonance spectral weight, which include spin anisotropy, reproduce this behavior yielding the magnitude of the spin anisotropy in these compounds.

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The spin (\(S\)) \(\frac{1}{2}\) two-dimensional (2D) square-lattice quantum Heisenberg antiferromagnet system has long been interesting to theoretical physicists due to the variety of transitions that can arise [1, 2, 3]. Moreover, the role of \(S = \frac{1}{2}\) fluctuations on a square lattice in the mechanism for cuprate superconductivity is hotly debated [3, 4, 5, 6]. The recently discovered family of H-bonded metal-organic magnets [7] offer the possibility to readily control the exchange parameters in a 2D system by changing chemical composition, thus creating spin architectures with desirable properties ‘to order’ [8]. For an idealized 2D system, long range magnetic order would not occur at finite temperature [2, 9]. However, in the metal-organic systems, interlayer coupling gives rise to a finite Neel temperature [10, 11, 12]. For these quasi-2D systems the ordering temperature is dominated by the weakest (the interlayer) exchange interaction, whereas the saturation magnetic field is dominated by the strongest exchange interactions, thus providing a means of estimating the spatial exchange anisotropy in the system [8]. It should be noted that the more 2D the system, the wider the temperature (\(T\)) range, \(T_N < T < J/k_B\), over which magnetic fluctuations dominate. Here we demonstrate that a spin anisotropy perturbation to the Heisenberg square lattice results in a new collective phenomenon within this regime, manifested as a shift in electron paramagnetic resonance (EPR) frequency at low temperature.

Fig. 1 illustrates the dramatic shift of the EPR magnetic field and line width with temperature for a single frequency, \(f\). Multi-frequency EPR measurements, fitted to \(f = f_0 + g\mu_B B/h\), where \(B\) is the resonance field, show that the shifts correspond to changes in both the low-field intercept \(f_0\) and effective \(g\)-factor \(g\). At high \(T\), \(f_0 = 0\), but as the phenomenon develops with decreasing \(T\), \(f_0\) becomes finite and positive, behavior that strongly resembles an energy gap opening. Not only is this unexpected in an \(S = \frac{1}{2}\) system; it is ruled out by the low temperature magnetization, which shows a monotonic increase between \(H = 0\) and the onset of saturation (see Fig. [1]). Any gap would be manifested as a region of reduced or zero \(dM/dH\) [8].

We shall show below that this dramatic change is not linked to the antiferromagnetic transition temperature in either of the compounds studied, but is rather related to the intralayer exchange interaction \(J\). The metal-organic compounds \([\text{CuHF}_2(\text{pyz})_2]\) \(\text{X}\) were therefore selected for this study as the choice of anion molecule \(\text{X}\) can alter \(J\) controllably by a factor \(\sim 2\) and because the \(J\)
values have been determined to a high accuracy using magnetometry \[8\]. In these compounds, Cu\(^{2+}\) ions are arranged in square-lattice layers, separated by pyrazine (pyz) molecules. The layers are held apart by bifluoride bridges \[7\,8\,12\]. Single crystals of \([\text{CuHF}_2(\text{pyz})_2]X\) with \(X = \text{ClO}_4\) or PF\(_6\), were produced by an aqueous chemical reaction between the appropriate Cu\(_2\) salt and stoichiometric amounts of the ligands (see \[7\,13\,14\] for preparation method details and X-ray data). Both materials undergo antiferromagnetic ordering, with \(T_N = 1.94\) K for \(X = \text{ClO}_4\) and \(T_N = 4.31\) K for \(X = \text{PF}_6\). Note that owing to differing summing conventions the definition of \(J\) used in the current paper is a factor two smaller than that in Ref. \[8\], i.e. herein \(J_{\text{plane}}(X = \text{ClO}_4) = 3.6\) K and \(J_{\text{plane}}(X = \text{PF}_6) = 6.2\) K.

EPR spectra of single-crystal samples were obtained in two ways. In the first method, the sample was placed in a cylindrical resonant cavity and the Q-factor and resonant frequency of the cavity were measured at each field point. The change in Q-factor is proportional to the microwave absorption of the sample \[15\]. These measurements were carried out in the frequency range 11-40 GHz using a Hewlett-Packard 8722ET network analyzer. The etalon was placed in a 31 K He system that was capable of stabilizing temperatures down to 1.5 K. For higher temperatures, the sample was placed in a confocal etalon resonator. The transmission, and hence change in microwave absorption, was measured in the frequency range 60-120 GHz using an ABmm \[16\] Millimetre wave Vector Network Analyser. The etalon was placed in a \(^3\)He system that was capable of stabilizing temperatures down to 0.6 K. For fixed temperatures, the EPR field was found to be a linear function of frequency, allowing the intercept and effective g-factor to be determined as described above; experimental values will be compared with theoretical predictions below.

Before demonstrating that the shift in intercept \(f_0\) and effective g-factor \(g\) (Fig. 1) is a collective phenomenon involving a large number of spins, we show that simpler models such as dimerization cannot account for the data. Fig. 2(a) illustrates the Zeeman splitting for non-interacting electrons and b) the corresponding linear frequency-magnetic field relationship with a zero frequency intercept \[15\]. Fig. 2(c) and d) includes the effect of an antiferromagnetic scalar exchange interaction \(J\). The \(|↑↑\rangle\), \(\frac{1}{\sqrt{2}}(|↑↓\rangle + |↓↑\rangle)\) and \(|↓↓\rangle\) states will be degenerate at \(B = 0\), with the \(\frac{1}{\sqrt{2}}(|↑↓\rangle - |↓↑\rangle)\) state separated by an energy \(-J\) \[15\]. Although this singlet-triplet gap causes the optically active (\(\delta S_z = ±1, \delta S_T = 0\)) EPR transitions within the triplet states to become ‘frozen out’ at \(T < J\), it does not introduce a gap across which optically active EPR transitions occur, which would lead to a finite frequency intercept.

Fig. 2(e) and f) includes a spin anisotropy in the exchange interaction, \(J_{zz} ≠ J_{xx} = J_{yy}\), lifting the zero field degeneracy of the \(S_{\text{Tot}} = 1, S_z = ±1\) and \(S_{\text{Tot}} = 1, S_z = 0\) states (Fig. 2), which in turn lifts the field degeneracy of the two intratriplet transitions, separating EPR lines 2 and 3. Although some of the possible EPR lines now have finite frequency \(B = 0\) intercepts, this simple model does not reproduce the systematics of the effect reported here. \(\frac{1}{\sqrt{2}}(|↑↓\rangle - |↓↑\rangle)\) is the groundstate so that the two transitions potentially observable at low temperature will be lines 1 and 4; however, for these to be optically-active, off-diagonal exchange terms (e.g. \(J_{xy}\)) such as the Dzyaloshinskyy-Moriya interaction must be present (since they mix the singlet and triplet states) \[15\]. We note that despite a Dzyaloshinskyy-Moriya term arising from a lower order spin-orbit perturbation than the diagonal spin anisotropy terms, that they are precluded by the inversion symmetry about the mid point of the dominant exchange interaction. At elevated temperatures \(T > J\), one would observe an EPR spectrum dominated by lines 2 and 3 (each with a finite \(B = 0\) intercept); as the sample cooled to \(T < J\), this would change to a spectrum dominated by the much weaker (or even absent) lines 1 and 4, with an intercept differing from that of 2 and 3. Such behavior does not lead to a smooth thermal evolution of the EPR line or the preservation of spectral weight to temperatures \(T < J\) that we observe.

Having shown that a simple local distortion cannot cause the effect shown in Fig. 1, we now turn to a finite cluster approach applied to an anisotropic 2D Heisenberg
model with spin anisotropy for two field orientations:
\[ H = J \sum S_i^x S_j^x + \Delta (S_i^z S_j^z + S_i^y S_j^y) - g_\perp \mu_B B \sum S_i^z, \]
where \( \Delta \) is the spin anisotropy, with \( \Delta = 1.0 \) being the isotropic (pure Heisenberg) case, \( \Delta < 1 \) an Ising-like or easy-axis antiferromagnet and \( \Delta > 1 \) an easy-plane \( x y \)-antiferromagnet. It should be noted that the input parameter to the model \( g_T \) is a temperature independent g-tensor that reproduces the high temperature \( T >> J \) g-factor anisotropy arising from the spin-orbit interaction. This g-anisotropy is consistent with the magnetic \( d_{x^2-y^2} \) orbital lying in the 2D planes [8]. \( J_\perp \) is assumed to be zero, since \( J_\perp << J_{\text{plane}} \), as demonstrated in [8]. This model was calculated using full diagonalization at finite temperature for 12, 14 and 16 sites [17]. There was little difference between the results with different numbers of sites, and therefore only the 14 site data are displayed here. The simulations were carried out for anisotropy values \( \Delta = 1.02, 1.04, 1.06 \) and 1.08. It was found that increased spin anisotropy leads to the parallel shift of the peak away from its initial position while at the same time the peak gains a finite width. Multiple smaller peaks in addition to the main peak were observed in the simulations for \( \Delta \neq 1 \), due to finite-size effects.

To compare the simulations to the results for \([\text{CuHF}_2(\text{pyz})_2]\text{ClO}_4\), the resonant magnetic field, Lorentz linewidth and spectral weight of the resonance were calculated for a resonance at 26 GHz. The resonant magnetic field was calculated as \( B_R = 2B_0 - \langle \omega \rangle \), where \( B_0 = 0.35J \) (26 GHz in units of \( J \)) and
\[ \omega \rangle = \frac{\int \omega S_{xx}(\omega, B_0)d\omega}{\int S_{xx}(\omega, B_0)d\omega}. \]
The Lorentz linewidth
\[ \Delta B \propto \sqrt{\frac{\omega_{\text{rel}}^2}{\omega_{\text{rel}}^4}}, \]
where \( \omega_{\text{rel}} = \omega - \langle \omega \rangle \). The spectral width was calculated as:
\[ I = \int \xi''(\omega_0, B)dB \sim (1 - e^{-\omega_0/T}) \int S_{xx}(\omega, B_0)d\omega \]
with the dynamic spin structure factor
\[ S_{xx}(\omega) = \frac{1}{N} \text{Re} \int_0^\infty e^{i\omega t} \langle S_x(t)S_x(0) \rangle dt. \]
A Lorentzian fit to the experimental data yielded the linewidth and spectral weight. As can be seen from Fig. 3, the results of the simulations reproduce the salient features of experimental results for \([\text{CuHF}_2(\text{pyz})_2]\text{ClO}_4\). The experimental values clearly lie between the simulated values of \( \Delta = 1.04 \) and 1.08. Taking into account the fact that above \( T = 0.8J \) the 1.04 simulation provides a good fit for both the position of the resonance and its linewidth, the best match for the data is given by a spin anisotropy of 1.04.

From Fig 3 the changes in the position and width of the EPR line in \([\text{CuHF}_2(\text{pyz})_2]\text{ClO}_4\), start as the temperature is lowered through 3.5 K; this corresponds to \( T/J = 1 \) (as opposed to \( T_N = 1.94 \text{ K} \)). Turning to \([\text{CuHF}_2(\text{pyz})_2]\text{PF}_6\), Fig. 4 shows that both \( g \) and \( f_0 \) undergo a dramatic change on cooling through 4.5 K. Coincidently, this is close to the ordering temperature \( T_N \) [8]. The greater relative thermal separation of \( T_N \) and \( T = J \) in the \text{ClO}_4 compound than in the \text{PF}_6 salt reflects the smaller interlayer exchange energy; one might say that the former is a closer approximation to two dimensionality than the \text{PF}_6 compound [8]. In spite of the proximity of the ordering temperature to the onset of the EPR shifts, the fit of the model to the data from the \text{PF}_6 compound that we will now give shows that it is the exchange interaction \( J \) that determines the temperature scale of the effect and not \( T_N \).

To compare the simulations for the results for \([\text{CuHF}_2(\text{pyz})_2]\text{PF}_6\) the experimental \( g \)-factors and frequency intercepts were calculated. The theoretical \( g \)-factors and intercepts are given by the slopes and intercepts of the \( \omega, B \) plots, which were obtained from the extrapolation through five calculated points, \( \omega/J = 1, 1.1, 1.2, 1.3, 1.4 \) for correspondence with the experimental frequency range.

In Fig. 4 we can see that the behaviour of the experimental \( g \)-factor and intercept are well matched by the simulations, with the dramatic difference between field \( B \) perpendicular to and \( B \parallel \) parallel to the square Cu plane being reproduced. For the \( B \parallel \) parallel data, the fact that we do not observe an upturn in the \( g \)-factor and the small positive intercept at low temperature is most likely due to a small angular misalignment (since the \( B \perp \) perpendicular effects are so much larger).

Considering the \( B \parallel \) perpendicular data, the \( g \)-factor experimental data suggests a spin anisotropy above 1.08, whereas the intercept data suggests an anisotropy close to 1.04. If we consider the corresponding data for \( X = \text{ClO}_4 \) (for which data was taken at only a few values due to the extreme weakness of the signal at low temperatures) we find that at \( T/J = 0.27 \) the experimental values are \( g = 0.96, g_0 \) and intercept = 0.12 \( J \). This gives a similar anisotropy, 1.06 - 1.04. For both materials it can be clearly seen that for \( T/J < 1 \) the experimental changes in both intercept and \( g \) factor are substantially more rapid than the simulations suggest. We propose that this is due to the experimental temperature scale being contracted relative to the theoretical temperature scale upon entering the ordered state, i.e., the phase transition has the effect of contracting the entropic (theoretical temperature) scale. The shape of the intercept curve suggests that the experimental value of the intercept has nearly stabilised by the lowest \( T/J \) values and therefore the intercept is taken to give the best indication of the
FIG. 3: A comparison of the experimental EPR data, circles, from [CuHF$_2$(pyz)$_2$]ClO$_4$ measured at 26 GHz with theoretical simulations, $\Delta =1.02$, 1.04, 1.06, 1.08, 1.10; solid, dot, dash, dot-dash and dot-dot-dash respectively. The left and bottom axes are absolute units, the right and top axes are renormalized by the exchange energy and spectroscopic $g$-factor. a) The variation of the magnetic field at which resonance occurs as a function of temperature. b) The linewidth (full width at half maximum of a Lorentzian fit) of the resonance peak as a function of temperature. c) The spectral weight (area under Lorentzian fit) normalized to its 15 K value. In all the cases error bars are smaller than data points.

spin anisotropy (around 1.04 in both compounds). The approximate conservation of spectral weight in both experimental and theoretical results also demonstrates the robustness of our model.

In conclusion we have observed a collective phenomenon in two members of the organic magnet system $(\text{Cu(HF}_2)(\text{pyz})_2)X$ that produces a shift in the frequency intercept of the EPR data which resembles, but does not correspond to, a gap opening in the system. Analogously to an anisotropic $g$-tensor, the spin anisotropy in the exchange interaction responsible for this effect most likely originates from spin-orbit coupling. As a result, this collective phenomenon is expected to be strongest for low-spin transition metal ions in relatively low symmetry environments, like the octahedral copper site $(3d^9)$ in $(\text{Cu(HF}_2)(\text{pyz})_2)X$. Although the organic systems investigated provide an ideal ‘low exchange energy scale’ environment in which to characterize this effect, strongly coupled copper octahedra are ubiquitous in correlated electron systems; for example, $J \approx 100$’s K in the parent phase of the high $T_c$ superconductors.

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