

Spin Configuration in the 1/3 Magnetization Plateau of Azurite Determined by NMR

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High magnetic field ^{63,65}Cu NMR spectra were used to determine the local spin polarization in the 1/3 magnetization plateau of azurite, Cu₃(CO₃)₂(OH)₂, which is a model system for the distorted diamond antiferromagnetic spin-1/2 chain. The spin part of the hyperfine field of the Cu2 (dimer) sites is found to be field independent, negative and strongly anisotropic, corresponding to ≈10% of fully polarized spin in a *d* orbital. This is close to the expected configuration of the quantum plateau, where a singlet state is stabilized on the dimer. However, the observed nonzero spin polarization points to some triplet admixture, induced by strong asymmetry of the diamond bonds *J*₁ and *J*₃.

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The natural mineral azurite, Cu₃(CO₃)₂(OH)₂, has been recently recognized [1] as a model system for the frustrated antiferromagnetic Heisenberg spin-1/2 chain of “distorted diamond” geometry defined in Fig. 1. Its most prominent feature is a large plateau in the magnetization curve at 1/3 of the saturation magnetization, which extends from 11 to 30 T when the applied magnetic field (*H*₀) is perpendicular to the chains. Such a “1/3 plateau” is usually associated with a classical collinear up-up-down (*uud*) type of spin arrangement, or rather to a quantum state which has this classical analogue. For example, a *uud* state is predicted for spins on a two-dimensional triangular lattice and observed in the Cs₂CuBr₄ compound [2]. The 1/3 plateau in azurite is proposed to be of fundamentally different, “00*u*” type, where the dominant *J*₂ coupling ensures that the two “dimer” spins on the Cu2 sites (see Fig. 1) are in a singlet state, while the third “monomer” (Cu1) spin is completely polarized by the field. As this state is based on the presence of a singlet, it is of pure quantum nature without a classical analogue. Azurite is a good candidate to be the first system exhibiting such a 1/3 plateau state, but a direct experimental evidence is still missing. The point is that both types of plateaus are predicted for a diamond chain, the 00*u* type driven by dominant *J*₂ coupling and an analogue of the *uud* state in presence of dominant *J*₁ and *J*₃ [3,4]. The azurite is close to the phase boundary between them, and there is a controversy on the *J* values proposed from the magnetization, specific heat and neutron scattering experiments [1,5–7]. The two different plateau types are distinguished by very different local spin polarizations, which can in principle be directly accessed by performing nuclear magnetic resonance (NMR) on the on-site copper ^{63,65}Cu nuclei. In this Letter we present such NMR data, which show that in the 1/3 plateau the dimer spins are nearly in the singlet configuration and thus confirm the 00*u* type of plateau. We find a small nonzero spin polarization of these sites, estimated to approximately 10% of full polarization, which points to an important asymmetry of *J*₁ and *J*₃ couplings.

The observed polarization is incompatible with a *uud* type of plateau, in which the dimer spins are strongly polarized.

In general, the copper NMR spectrum of a single crystal consists of 6 NMR lines per each nonequivalent Cu site, corresponding to three transitions between energy levels of a spin *I* = 3/2 nucleus for each of the two ⁶³Cu and ⁶⁵Cu isotopes. In the crystallographic structure of azurite, shown in Fig. 1, we recognize two different copper sites in two equivalent chains of different orientation with respect to the arbitrary direction of the applied magnetic field **H**₀(*α*). We also note that the two Cu2 sites of each dimer are expected to be undistinguishable by NMR, which is en-

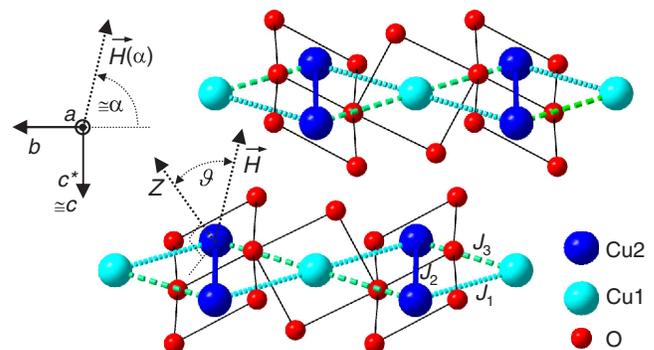


FIG. 1 (color online). Diamond chains formed by the exchange interactions, $J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j$, between $S = 1/2$ spins of Cu²⁺ ions in the crystal structure of azurite. There are two equivalent but differently oriented chains, related by the *ac* plane of mirror symmetry. Chains contain monomer spins on the Cu1 sites coupled by *J*₁ and *J*₃ interactions to each spin of the dimer formed by the two Cu2 sites, mutually coupled by *J*₂. There is an inversion symmetry on each Cu1 site and at the center of each dimer. For each Cu site 4 nearest neighboring oxygen atoms (connected by thin lines) define approximately the plane of the local symmetry of the wave functions and of the corresponding EFG tensor. Dotted line vectors define the rotation angle *α*, and the angle *θ* between the magnetic field and the *Z* principal axis of the EFG tensor. C and H atoms are not shown.

sured by the inversion symmetry with respect to the center of each dimer. We thus expect that $^{63,65}\text{Cu}$ NMR spectrum has $6 \times 2 \times 2 = 24$ NMR lines. Single crystal spectra presented in Fig. 2 contain only 12 lines, meaning that we observe only one of the two Cu sites. We recall that these spectra are taken in the plateau phase, so that they are not affected by the Néel ordering appearing at 1.9 K at field values *below* the plateau phase [8]. A standard way for the identification of the observed site is to compare the symmetry of the local electric field gradient (EFG) tensor determined by NMR to what is expected from the local symmetry of the four nearest neighboring (NN) oxygen atoms (see Fig. 1). This rather technical procedure, explained in detail in the following paragraph, unambiguously demonstrates that only Cu2, i.e., the dimer site, is observed by NMR.

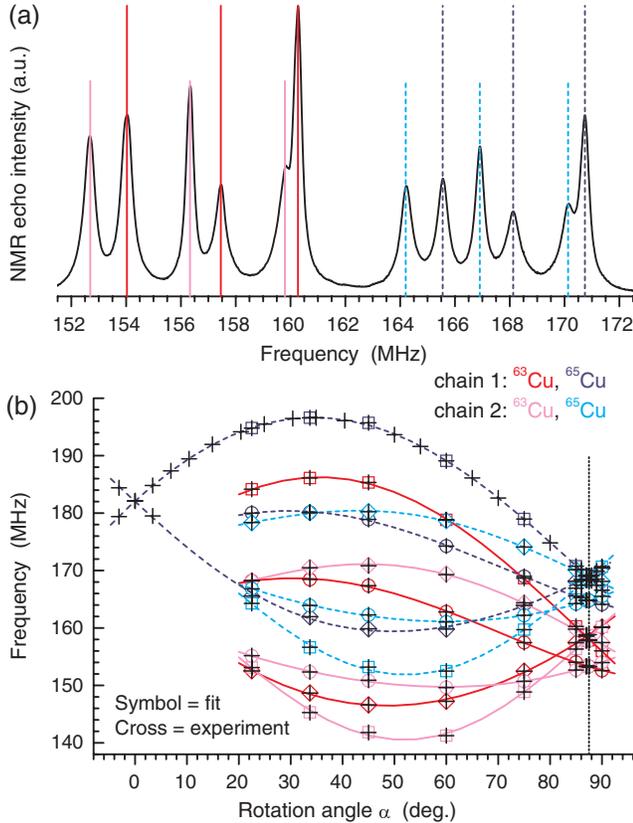


FIG. 2 (color online). Rotation dependence of copper NMR spectra of azurite at $T = 1.5$ K. Magnetic field of 15.0 T is applied perpendicular to the rotation axis that was close to the crystal a axis. (a) NMR spectrum taken at $\alpha = 85^\circ$ and the corresponding fit (vertical lines), as explained in the text. (b) Angular dependence of the observed line positions (crosses, with lines to guide the eye) and the corresponding fits (open symbols: circles for the central transitions and squares and diamonds for the satellites). Color code is given in the figure: dark (light) gray lines for the chain 1 (2) and solid (dashed) lines for the $^{63(65)}\text{Cu}$ isotope. Vertical dotted line denotes $H_0 \parallel ac$ plane orientation, where both chains are identical.

Each copper isotope ($I = 3/2$) generates a triplet of NMR lines whose average frequency reflects the Zeeman coupling to the total “effective” magnetic field \mathbf{H}_{eff} , while the line splitting is induced by the “quadrupolar” coupling to the local EFG. The corresponding nuclear spin Hamiltonian, $\mathcal{H} = \hbar\gamma\mathbf{I} \cdot \mathbf{H}_{\text{eff}} + h\nu_Q[3I_z^2 - I(I+1) + \eta(I_x^2 + I_y^2)]/6$, is uniquely defined by 5 parameters: the EFG tensor described by the quadrupolar coupling ν_Q and its asymmetry parameter η , and H_{eff} and its direction ($\vartheta_{\text{EFG}}, \varphi_{\text{EFG}}$) with respect to the principal axes (X, Y, Z) of the EFG tensor [9]. Knowing the gyromagnetic ratios for the two isotopes, $^{63}\gamma$ and $^{65}\gamma$, as well as the ratio of their quadrupolar couplings, $^{63}\nu_Q/^{65}\nu_Q = 1.0805$, these 5 parameters can be fit to provide the observed 6 NMR frequencies (for each chain). The ν_Q and η parameters do not depend on the orientation of magnetic field and, in particular, they are common to spectra from two chains shown in Fig. 1. In this experiment we performed *in situ* rotation of the crystal around the axis that was close to the crystal a axis, and have taken several complete spectra at different rotation angles α (see Fig. 1), as shown in Fig. 2. The smallest NMR line widths and thus the most precise fits are obtained when $\vartheta_{\text{EFG}} \cong 90^\circ$, which for chain 1 corresponds to $\alpha \cong 45^\circ$. This particular orientation has therefore been used to determine $^{63}\nu_Q = 36.5$ MHz and $\eta = 0.085$, and the obtained EFG values have been successfully used to produce *all* the other fits—this time by fitting only three parameters ($H_{\text{eff}}, \vartheta_{\text{EFG}}, \varphi_{\text{EFG}}$) for each set of 6 NMR frequencies (see Fig. 2). The experimentally obtained $\vartheta_{\text{EFG}}(\alpha)$ dependence could then be compared to a simple approximate estimate for this quantity, based on the crystallographic structure. We know that for an ideal tetragonal coordination a pure $d_{x^2-y^2}$ orbital pointing towards 4 NN oxygens generates axially symmetric EFG with the strongest principal axis along the Z direction. Therefore, the best estimate for the Z axis is the normal to the plane approximately defined by 4 NN oxygens (see Fig. 1). The direction of \mathbf{H}_{eff} is approximated by the direction of the applied field, supposing that the rotation axis is precisely the a axis of the crystal. These estimates of Z and \mathbf{H}_{eff} directions define the angle $\vartheta_{\text{Theory}}$, and its rotation dependence $\vartheta_{\text{Theory}}(\alpha)$ is plotted in Fig. 3 for both Cu sites and both chains, in comparison with the experimental $\vartheta_{\text{EFG}}(\alpha)$ values. Neglecting small offset due to various approximations, from these data one clearly identifies that the observed NMR signal corresponds to dimer Cu2 sites and is incompatible with the Cu1 sites.

The principal information obtained from the fits is the spin part of the hyperfine field, $\mathbf{H}_{\text{spin}} = \mathbf{H}_{\text{eff}} - (1 + \mathbf{K}_{\text{orb}})\mathbf{H}_0 = \mathbf{A}g\mu_B\langle\mathbf{S}\rangle$, induced by the local spin polarization $\langle\mathbf{S}\rangle$ through the hyperfine coupling tensor \mathbf{A} . The orbital (Van Vleck) shift tensor \mathbf{K}_{orb} is here a minor correction, because typical \mathbf{A} values for a copper spin are as large as $A_Z \approx -20$ T/ μ_B , with large anisotropy $A_Z/A_\perp \approx 10$. Knowing that the EFG and the hyperfine shift tensors are dominantly determined by the same wave function, we

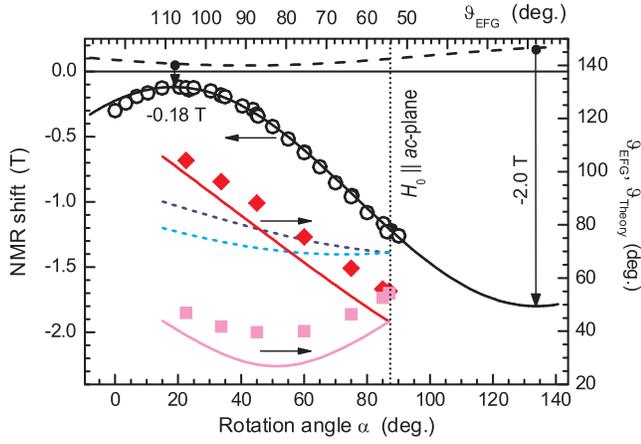


FIG. 3 (color online). Left scale (black lines and symbols): rotation dependence of the NMR shift obtained from the highest frequency ^{65}Cu NMR line (open circles), the fit to these data (solid line) and an estimate of the orbital shift (dashed line). These results provide an estimate of the hyperfine field $H_{\text{spin}}^{\parallel} \approx -2.0$ T and its anisotropy $H_{\text{spin}}^{\parallel}/H_{\text{spin}}^{\perp} \approx 11$, which corresponds to 10% spin polarization in a d orbital. Right scale (color/gray scale lines and symbols): ϑ_{EFG} deduced by fitting the line positions shown in Fig. 2(b) (solid squares and diamonds), following closely the predictions for the dimer Cu2 site (solid lines) and not the Cu1 site (short-dashed lines), as explained in the text. Experimental $\vartheta_{\text{EFG}}(\alpha)$ dependence (diamonds) is used to define the upper horizontal scale.

expect that the principal axes of both tensors are approximately the same, so that the H_{spin} vs ϑ_{EFG} dependence provides a complete information on the local spin polarization. In Fig. 3 we have plotted the rotational dependence of the experimental NMR line shift ($H_{\text{eff}} - H_0$) and its extrapolation by a sinusoidal fit, together with an estimate of the orbital shift ($K_{\text{orb}}^Z \approx 1.3\%$, $K_{\text{orb}}^{\perp} \approx 0.3\%$). From these data we estimate the spin-induced hyperfine field to be $H_{\text{spin}}^{\parallel} \approx -2.0$ T, with an anisotropy $H_{\text{spin}}^{\parallel}/H_{\text{spin}}^{\perp} \approx 11$ (where \parallel and \perp refer to the principal axes of this tensor). This corresponds to about 10% spin polarization of a typical Cu^{2+} $d_{x^2-y^2}$ orbital. The error in these values is estimated to be $\approx 20\%$, dominantly from the extrapolation of the angular dependence to $H_{\text{spin}}^{\parallel}$ [10]. In particular, in Fig. 3 we clearly see that the maximum of the experimental line shift is shifted by 18° from the expected $\vartheta_{\text{EFG}} = 90^\circ$ value. This means that the principal axes of the EFG and the hyperfine tensors are not really parallel, pointing to a departure from the simplified picture of pure $d_{x^2-y^2}$ orbital. Indeed, the electronic density observed by x-ray diffraction suggests significant admixture of other orbitals [11].

In a true magnetization plateau the magnetization should not vary with the magnetic field. In order to test this most prominent feature of the plateau in azurite, we performed very high field measurements of the copper NMR spectra, in the field range 17–28 T and at 1.4 K, for \mathbf{H}_0 applied close

to the c axis. Because the effects of the quadrupolar coupling and the hyperfine shift are entangled in the NMR spectra, the shift can only be determined by the complete NMR fits as explained in the third paragraph. The line positions and fits shown in Fig. 4 indeed confirm that H_{spin} is to a high precision field independent in the plateau. For a field variation from 19 to 26 T (i.e., 37%) the change in the measured $|H_{\text{spin}}|$ is found to be $(1 \pm 1)\%$, where the precision is limited by our estimate of the orbital shift tensor. This information might be important to constrain the possible effects of Dzyaloshinski-Moria (DM) interaction terms, which may induce some weak field dependence of the spin polarizations. The DM interaction on the dimer bond has been invoked to explain strong anisotropy of the width of the plateau [1]. However, the presence of an inversion center at the center of the dimer precludes such a term, and only DM interaction on J_1 and J_3 exchange paths are possible. Whether or not they can explain the observed anisotropy has not yet been studied theoretically.

Despite considerable efforts, we could not observe the NMR signal from the monomer Cu1 spin. We have tried to find it at very low temperature in order to minimize the spin fluctuations. In this way the longitudinal (T_1^{-1}) relaxation rate was reduced, however, the same does not necessarily apply to the transverse (T_2^{-1}) relaxation [12]. To provide the correct total polarization of the $1/3$ plateau, the spin polarization at the Cu1 site has to be $\approx 80\%$, that is ≈ 8 times more than at the dimer sites. We can then roughly estimate that the corresponding T_2^{-1} ratio is of the order of

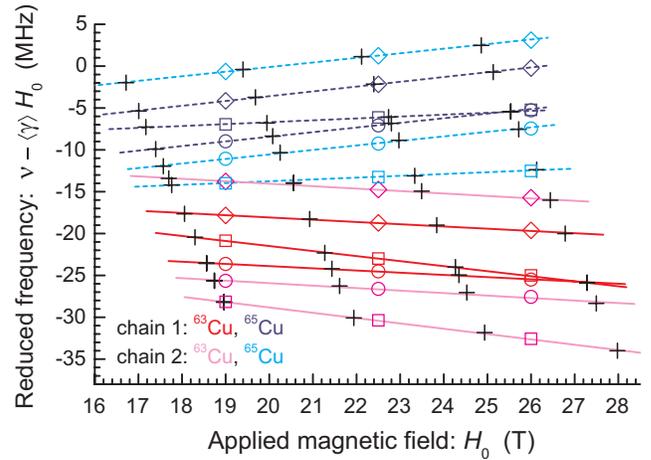


FIG. 4 (color online). Magnetic field dependence of the $^{63,65}\text{Cu}$ NMR line positions in azurite at 1.4 K, for the field orientation close to the c axis. The spectra were taken at constant frequency by sweeping the field, and results plotted in the reduced frequency scale to eliminate the dominant field dependence $\langle\gamma\rangle H_0$, with $\langle\gamma\rangle = (\gamma^{63} + \gamma^{65})/2 = 11.687$ MHz/T. Lines are linear fits to the observed field dependence, and symbols fits to this linear interpolation at 19, 22.5, and 26 T, which confirm that the spin polarization of the dimer Cu2 site is magnetic field independent. Color and symbol code is the same as in Fig. 2.

$8^2 = 64$. As the dimer T_2 values are in the 10–100 μs range (depending on the orientation), this factor is enough to reduce the Cu1 T_2 below the experimental dead time for the observation of an NMR signal. This provides a reasonable explanation why Cu1 spin could not be observed, but also an important hint on the system: the longitudinal spin fluctuations (effective in T_2 relaxation) are probably not gapped.

Finally, we remark that here we have considered only the standard on-site hyperfine coupling to the copper spin, and not the transferred hyperfine coupling which could in principle couple the observed nuclear spin at the dimer site to the neighboring (strongly polarized) monomer spin. This latter mechanism typically relies on almost negligible admixture ($\sim 1\%$) of the on-site s -wave orbital in the extended Wannier wave function belonging to the neighboring electronic spin. While the on-site spin polarization induced in this way is negligible ($\sim 1\%$), very high hyperfine coupling of an s -wave orbital ($\sim 200 \text{ T}/\mu_B$) can in principle provide significant transferred hyperfine field. However, this field is positive and isotropic, in obvious contradiction to what is observed in azurite. Negative and strongly anisotropic H_{spin} necessarily implies significant on-site spin polarization of the Cu orbital.

To provide a simple discussion for the observed polarization of dimer spins, we note that the approximate wave functions proposed for the $1/3$ plateau of the diamond chain [3] can be generalized to represent an arbitrary mixture of the three single-spin-flip states, $\Psi(\mp, \beta) = \cos\beta[|\uparrow\uparrow\rangle \mp |\uparrow\downarrow\rangle]/\sqrt{2} - \sin\beta|\downarrow\downarrow\rangle$, which by construction has correct total and local spin polarization of μ_B and $\mu_B \times (\sin^2\beta, \sin^2\beta, \cos^2\beta - \sin^2\beta)$, respectively. In particular, there is equal spin polarization on the two dimer spins. In this notation the two reference plateau states [3] are $00u = \Psi(-, 0)$ and $uud = \Psi(+, \arccos(1/\sqrt{3}))$, where the sign difference corresponds to the different symmetry. (Note that at least two unit cells should be taken into account to properly represent all symmetries of the system.) Using $\Psi(\mp, \beta)$ as a trial function to minimize the energy by optimizing β , one can easily see that the pure singlet $00u$ ($\beta = 0$) state is obtained only for the symmetric diamond couplings $J_1 = J_3$, while deviation from this case necessarily leads to some admixture of the triplet, meaning some nonzero polarization of the dimer spins ($\beta \neq 0$). Observed polarization on the dimer site means that this admixture is significant, $\sin\beta \approx \sqrt{0.1} \approx 0.3$ [13], and thus should correspond to an important asymmetry of couplings. A correct estimate of the corresponding J coupling values should rely on numerical solutions of the spin Hamiltonian, relating the observed spin polarization to the corresponding constraint on the J couplings, say the J_3/J_1 vs J_2/J_1 dependence [14]. Two available points predicting the correct local spin polarization, $J_3/J_1 = -0.5$ [13] and $+0.4$ [14], show that from NMR we cannot directly conclude if one of the couplings is ferromagnetic or not. However, if NMR data are combined with other con-

straints, as the width of the plateau from the magnetization data [1] and the energy of excitations from the neutron scattering data [6], one should clearly define the couplings, or indicate whether the diamond chain model is too simple to describe azurite. Here we recall a possible influence of interchain couplings.

In conclusion, by copper NMR in the $1/3$ magnetization plateau of azurite we have determined the local spin polarization of the dimer spins to be $\approx 0.1\mu_B$. This provides the first direct evidence for a quantum type of a $1/3$ plateau having *no* classical analogue, which consists of dimers in a singlet state and fully polarized monomers. The deviation from ideal zero polarization of the dimer implies important asymmetry of the diamond couplings, $J_1 \neq J_3$, and provides a strong constraint for the determination of their values.

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