

Nuclear magnetic resonance evidence for a strong modulation of the Bose-Einstein condensate in BaCuSi₂O₆

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We present a ^{63,65}Cu and ²⁹Si NMR study of the quasi-2D coupled spin 1/2 dimer compound BaCuSi₂O₆ in the magnetic field range 13–26 T and at temperatures as low as 50 mK. NMR data in the gapped phase reveal that below 90 K different intradimer exchange couplings and different gaps ($\Delta_B/\Delta_A=1.16$) exist in every second plane along the *c* axis, in addition to a planar incommensurate (IC) modulation. ²⁹Si spectra in the field induced magnetic ordered phase reveal that close to the quantum critical point at $H_{c1}=23.35$ T the average boson density \bar{n} of the Bose-Einstein condensate is strongly modulated along the *c* axis with a density ratio for every second plane $\bar{n}_A/\bar{n}_B \approx 5$. An IC modulation of the local density is also present in each plane.

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The interest in Bose-Einstein condensation (BEC) has been considerably renewed since it was shown to occur in cold atomic gases.¹ In condensed matter, a formal analog of the BEC can also be obtained in antiferromagnetic (AF) quantum spin systems^{2–5} under an applied magnetic field. Many of these systems have a collective singlet ground state, separated by an energy gap Δ from a band of triplet excitations. Applying an external magnetic field (*H*) lowers the energy of the $M_z=-1$ subband and leads to a quantum phase transition between a gapped nonmagnetic phase and a field induced magnetic ordered (FIMO) phase at the critical field H_{c1} corresponding to $\Delta_{\min}-g\mu_B H_{c1}=0$, where Δ_{\min} is the minimum gap value corresponding to some \mathbf{q} vector \mathbf{q}_{\min} . This phase transition, provided the U(1) symmetry is conserved, can be described as a BEC of hard core bosons in which $H-H_{c1}$ controls the boson density at a given temperature *T*.^{2–5} Quite often, however, anisotropic interactions can change the universality class of the transition and open a gap.^{6–8} From that point of view, BaCuSi₂O₆ (Ref. 9) seems a very promising candidate for the observation of a true BEC quantum critical point (QCP).¹⁰ In addition, this system exhibits an unusual dimensionality reduction at the QCP, which was attributed to frustration between adjacent planes in the nominally body-centered-tetragonal structure.¹¹ The material also exhibits a weak orthorhombic distortion at ≈ 90 K, which is accompanied by an in-plane incommensurate (IC) lattice modulation.¹² This structural phase transition affects the triplon dispersion, and several scenarios for a modulation of the amplitude of the BEC along the *c* axis have been proposed on the basis of low field inelastic neutron data.¹³

In order to get a microscopic insight of this system, we performed ²⁹Si and ^{63,65}Cu NMR in BaCuSi₂O₆ single crystals. Our data in the gapped phase reveal that the structural phase transition at ≈ 90 K not only introduces an IC distortion within the planes, but also leads to the existence of two types of planes alternating along the *c* axis. From one plane to the other, the intradimer exchange coupling and the energy gap for the triplet states differ by 16%. Exploring the vicinity of the QCP in the *T* range 50–720 mK, we confirm the linear

dependence of T_{BEC} with $H-H_{c1}$ as expected for a two-dimensional (2D) BEC. Our main finding is that the average boson density \bar{n} in the BEC is strongly modulated along the *c* axis in a ratio of the order of 1:5 for every second plane, whereas its local value $n(\mathbf{R})$ is IC modulated within each plane.

NMR measurements have been performed on ~ 10 mg single crystals of BaCuSi₂O₆ with *H* applied along the *c* axis. The investigation of the FIMO phase was conducted in a 20 MW resistive magnet at the GHMFL in the *H* range 22–25 T and the *T* range 50–720 mK. Except for a few field sweeps in the gapped phase, the spectra were obtained at fixed fields by sweeping the frequency in regular steps and summing the Fourier transforms of the recorded echoes.

Before discussing the microscopic nature of the QCP, let us first consider the NMR data in the gapped phase. The system consists of $S=1/2$ Cu spin dimers parallel to the *c* axis and arranged (at room temperature) on a square lattice in the *ab* plane. Each Cu dimer is surrounded by four Si atoms, lying approximately in the equatorial plane. For Cu nuclei, the interaction with the electronic spins is dominated by the on-site hyperfine interaction. For ²⁹Si nuclei both the transferred hyperfine interaction through oxygen atoms with a single dimer and the direct dipolar interaction are important. According to the room temperature structure $I4_1/acd$,¹⁴ there should be only one single Cu and two nearly equivalent Si sites for NMR when $H\parallel c$. As far as ²⁹Si is concerned, one actually observes a single line above 90 K, as can be seen in Fig. 1. However, below 90 K, the line splits into two components, each of them corresponding to an IC pattern, that is an infinite number of inequivalent sites. This corresponds to the IC structural phase transition discovered by x-ray measurements.¹² At 3 K, when *T* is much smaller than the gap, the spin polarization is zero and one observes again a single unshifted line, at the frequency $\nu=\nu_0=^{29}\gamma H$ defined by the Si gyromagnetic ratio ²⁹ γ .

In the ^{63,65}Cu NMR spectra recorded at 3 K and 13.2 T (Fig. 2), however, one can distinguish *two* different Cu sites, denoted A and B. That is, each of the six lines of the Cu

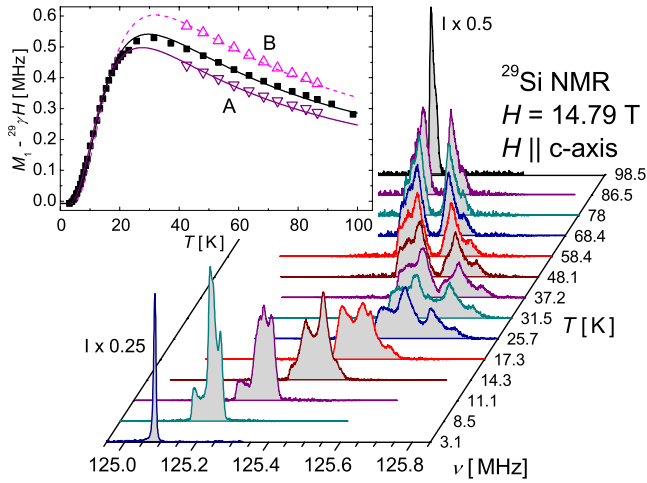


FIG. 1. (Color online) Evolution of the normalized ^{29}Si NMR spectra as a function of T in the gapped phase. Below 90 K the line splits into two components, each of them corresponding to an IC pattern. Inset: T dependence of the first moment (i.e., the average position) for (i) the total spectra (squares) and (ii) the individual components before they overlap (up and down triangles). The solid and dashed lines are fits for noninteracting dimers.

spectrum (for two copper isotopes \times three transitions of a spin 3/2 nucleus) is split into two, which is particularly obvious on the lowest frequency “satellite” ^{63}Cu line. The whole spectra can be nicely fitted with the following parameters: $^{63}\nu_Q^{A(B)} = 14.85$ (14.14) MHz, $\eta = 0$, and $K_{zz}^{A(B)} = 1.80$ (1.93)%, where ν_Q is the quadrupolar frequency and η is the asymmetry parameter. The K_{zz} is the hyperfine shift, expected to be purely orbital since the susceptibility has fully

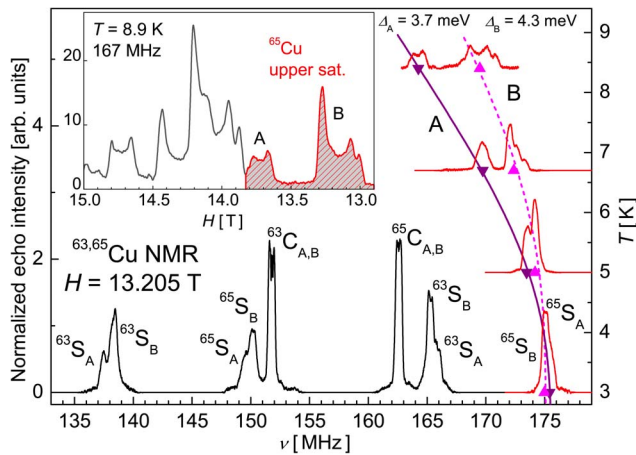


FIG. 2. (Color online) $^{63,65}\text{Cu}$ NMR spectra of $\text{BaCuSi}_2\text{O}_6$ in the gapped phase, well below the critical field. The T dependence of the high-frequency “satellite” line clearly reveals two different copper sites. From their shifts, the two corresponding gap values have been determined. Inset: field sweep spectrum that reveals the IC nature of the line shape for each of the two sites. Shading separates the contribution of the ^{65}Cu high-frequency satellite from the rest of the spectrum. The analysis of the latter part confirms that the observed line shape has a pure magnetic origin.

vanished.¹⁵ On increasing T the highest frequency ^{65}Cu “satellite” lines of sites A and B become well separated and both exhibit a typical IC line shape. Although the apparent intensities of lines A and B look different, they correspond to the same number of nuclei after corrections due to their different spin-spin relaxation rates $1/T_2$. Since the satellite NMR lines at 3 K (the lowest temperature) are narrow, the modulation of ν_Q is negligible, meaning that the IC line shapes visible at higher temperature are purely magnetic. This is confirmed by the analysis of the spectrum shown in the inset of Fig. 2, which shows that at 8.9 K the broadening of the “central” line is the same as that observed on the “satellites.” Such a broadening results from a distribution of local hyperfine fields: $\delta h_z(\mathbf{R}) = A_{zz}(\mathbf{R})m_z(\mathbf{R})$ in which $A(\mathbf{R})$ is the hyperfine coupling tensor and $m_z(\mathbf{R})$ is the longitudinal magnetization at site \mathbf{R} . Since $\nu_Q(\mathbf{R})$ is not modulated by the distortion, one expects that the modulation of $A(\mathbf{R})$ is negligible too, $A(\mathbf{R}) = A$. The NMR line shape thus directly reflects the IC modulation of m_z in the plane.

Keeping constant the ν_Q parameters obtained at 3 K, one can analyze the T dependence of the shift $K_{zz}^\alpha(T)$ of each component $\alpha = A$ or B according to $K_{zz}^\alpha(T) - K_{zz}^\alpha(0) = A_{zz}^\alpha m_z^d(\Delta_\alpha, H, T)/H$. Here m_z^d is the magnetization of a non-interacting dimer, $m_z^d = g_c \mu_B / (e^{(\Delta_\alpha - g_c \mu_B H)/k_B T} + 1)$ in the given T range, $g_c = 2.3$,¹⁶ and K_{zz}^α is determined from the average line position, i.e., the first moment. The best fit was obtained for $\Delta_{A(B)} = 3.7(4.3)$ meV and $A_{cc}^{A(B)} = -16.4$ T/ μ_B . We assumed that $A_{cc}^A = A_{cc}^B$, but the values of Δ depend only weakly on this quantity. The values are slightly higher than those determined by neutron inelastic scattering for $\mathbf{Q}_{\min} = [\pi, \pi]$,¹³ which is normal considering our approximate description. However, the ratio $\Delta_B/\Delta_A = 1.16$ is in excellent agreement with the neutron result 1.15. Considering the fact that there is no disorder in the system (as Cu lines at low T are narrow), and that x rays did not detect any commensurate peak corresponding to a doubling of the unit cell in the ab plane, our NMR data can only be explained if there are *two types of planes* with different gap values. Furthermore, a careful examination of satellite B in the inset of Fig. 2 reveals a more complicated structure than for satellite A. This very likely results from the existence of two slightly different types of planes B and B', in agreement with neutron findings of three different triplet modes.¹³ Since A and B satellites correspond to the same number of Cu nuclei, there must be four types of planes in the unit cell. Hereafter, we shall neglect this small difference and only refer to type A and B planes. Looking back at the ^{29}Si spectra in Fig. 1, one also observes just below 90 K two well separated components, both of them exhibiting an IC pattern. They indeed correspond to the two types of planes, as the T dependence of their positions can be well fit using values close to Δ_A and Δ_B determined from Cu NMR (inset to Fig. 1). This means that the 90 K structural phase transition not only corresponds to the onset of an IC distortion in *every* ab plane, but also leads *simultaneously* to an alternation of different planes along the c axis,¹⁷ with intradimer exchange in the ratio $J_B/J_A \cong \Delta_B/\Delta_A = 1.16$.

Let us now recall what is expected from a microscopic point of view in the vicinity of the QCP corresponding to the onset of a *homogeneous* BEC for coupled dimer systems.

As soon as a finite density of bosons n is present ($H > H_{c1} = \Delta_{\min}/g\mu_B$), a transverse staggered magnetization m_{\perp} (\perp to H) appears. Its amplitude and direction correspond respectively to the amplitude and phase of the order parameter. At the same time, the longitudinal magnetization m_z is proportional to the number of bosons at a given temperature and field. Due to the appearance of a static \mathbf{m}_{\perp} , the degeneracy between sites which were equivalent outside the condensate will be lifted and their corresponding NMR lines will be split into two. To be more specific, we consider a pair of Si sites situated in the ab plane on opposite sides of a Cu dimer. Outside the condensate, and in the absence of the IC modulation, they should give a single line for $H \parallel c$. Inside the condensate the NMR lines of this pair of Si sites will split by $\pm^{29}\gamma|A_{z\perp}|m_{\perp}$ because their $A_{z\perp}$ couplings are of opposite sign. Obviously, observing a splitting of lines requires the existence of off-diagonal terms in the hyperfine tensor. Such terms are always present due to the direct dipole interaction between an electronic and the nuclear spin, which can be easily calculated.

Instead of this expected simple line splitting, the spectra of Fig. 3(a) reveal a quite complex modification of the line shape when entering the condensate. The narrow single line, observed at 23.41 T at the frequency ν_0 , which corresponds to a negligible boson density, suddenly changes into a composite line shape including a narrow and a broad component. The spread-out of the broad component increases very quickly with the field. The width of the narrow component also increases, but at a much lower rate. Both peculiar broadenings are related to the IC modulation of the boson density $n(\mathbf{R})$ due to the structural modulation. A copper dimer at position \mathbf{R} has in total four Si atoms (denoted by $k=0,1,2,3$) situated around in a nearly symmetrical square coordination. The absolute values of the corresponding hyperfine couplings will thus be nearly identical, and we will also neglect their dependence on \mathbf{R} . These four Si sites will give rise to four NMR lines at the frequencies $^{29}\nu_k(\mathbf{R}) = \nu_0 + \nu_1(\mathbf{R}) + \nu_{2,k}(\mathbf{R})$, where $\nu_1(\mathbf{R}) = ^{29}\gamma A_{zz}g\mu_B n(\mathbf{R})$ and $\nu_{2,k}(\mathbf{R}) = ^{29}\gamma A_{z\perp}m_{\perp}(\mathbf{R})\cos(\phi - k\pi/2)$. Note that $\nu_{2,k}$ only exists when the bosons are condensed, that is, when there is a transverse magnetization m_{\perp} pointing in the direction ϕ . In a uniform condensate m_{\perp} is proportional to \sqrt{n} near the QCP, since the mean field behavior is valid in both two and three dimensions. We assume that only the amplitude of the order parameter is spatially modulated, and that $m_{\perp}(\mathbf{R}) \propto \sqrt{n(\mathbf{R})}$. The line shape is the histogram of the distribution of $^{29}\nu_k(\mathbf{R})$, convoluted by some broadening due to nuclei-nuclei interaction.

Three quantities can be derived from the analysis of NMR lines at fixed T values and variable H : the spatial average of the boson density $\bar{n}(H, T)$, the field $H_{c1}(T)$ corresponding to the BEC phase boundary, and the field dependence of the BEC order parameter (for T close to zero). $\bar{n} = \bar{m}_z/g\mu_B$ is directly proportional to the first moment of the line $M_1 = \int_{-\infty}^{\infty} (\nu - \nu_0)f(\nu)d\nu = ^{29}\gamma A_{zz}g\mu_B \bar{n}(H, T)$, where the line shape $f(\nu)$ is supposed to be normalized.¹⁸ The second moment (i.e., the square of the width) of the line $M_2 = \int_{-\infty}^{\infty} (\nu - \nu_0 - M_1)^2 f(\nu)d\nu$ has two origins: the broadening due to the IC distribution of $[n(\mathbf{R}) - \bar{n}]$, and that due to the onset

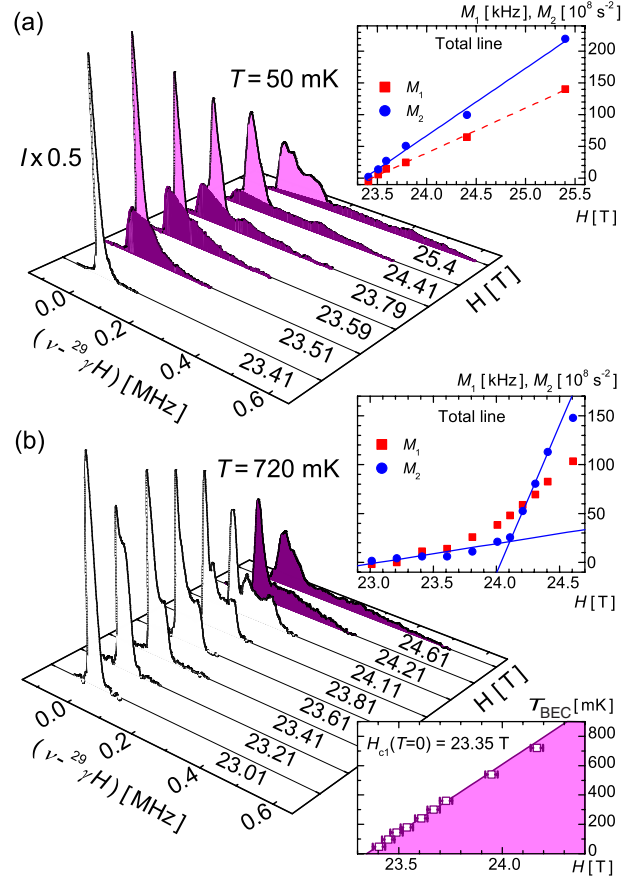


FIG. 3. (Color online) Evolution of the normalized ^{29}Si spectrum as a function of H at fixed T . The colored spectra correspond to the BEC. (a) $T=50$ mK: Instead of a simple splitting of the line as expected for a standard BEC, a complex pattern appears, typical of an IC distribution of the local hyperfine field. Inset: H dependence of the first (M_1 , squares) and second (M_2 , circles) moment of the spectra. M_1 is proportional to m_z and M_2 to the square of the order parameter. (b) $T=720$ mK: The nonzero magnetization outside the BEC leads to an IC pattern for fields $H \leq H_{c1}(T)$, where $H_{c1}(T)$ is determined from the H dependence of M_2 , as shown in the inset. Lower inset: T_{BEC} is linear in $H - H_{c1}$, as expected for a 2D BEC QCP.

of $m_{\perp} \propto \sqrt{n(\mathbf{R})}$ in the condensate. When increasing H at $T \approx 0$, the condensation occurs as soon as bosons populate the dimer plane. This is observed in the inset of Fig. 3(a) at $T=50$ mK. Both M_1 (\bar{n}) and M_2 (m_{\perp}) vary linearly with the field and the extrapolation of M_2 to zero allows the determination of H_{c1} at 50 mK. For higher temperatures a thermal population of bosons \bar{n} exists and increases with H before entering the BEC phase. As a result both M_1 and M_2 increase nonlinearly with H , as shown in the upper inset of Fig. 3(b). However, the increase of $M_2(H)$ shows two clearly separated regimes and allows the determination of $H_{c1}(T)$ as the point where the rate of change of $M_2(H)$ strongly increases due to the appearance of m_{\perp} . Applying this criterion to all temperatures, we were able to determine the field dependence of T_{BEC} [lower inset of Fig. 3(b)] and define precisely the QCP at $H_{c1} = 23.35$ T. In agreement with the torque measurements,¹¹ we find a linear field dependence. This is

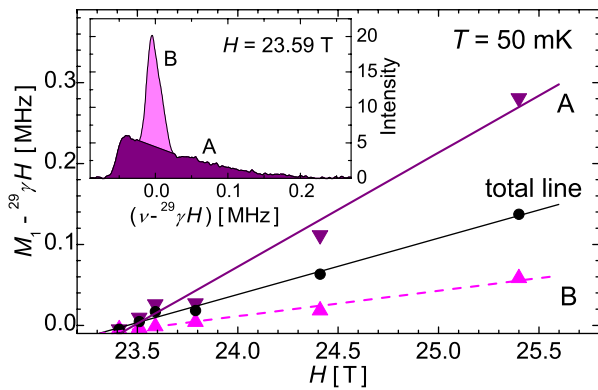


FIG. 4. (Color online) Using a simple decomposition of the spectra into two components as shown in the inset, we determined the 1st moments of the ^{29}Si lines corresponding to the different types of planes A and B. From the slopes of their field dependence, the ratio of the average boson density is found equal to $\bar{n}_A/\bar{n}_B \approx 5$.

the signature of a 2D BEC QCP, where $T_c \propto (H - H_{c1})^\phi$ with $\phi = 2/d$ and $d = 2$.¹⁹

This analysis, however, does not take into account the specificity of the line shapes, which are related to the existence of two types of planes with different energy gaps. A careful examination of the spectra clearly reveals that they correspond to the superposition of two lines exhibiting different field dependence at fixed T value. For the sake of simplicity, we have made a decomposition only for the spectra at 50 mK, as shown in the inset of Fig. 4. Clearly, one of the components remains relatively narrow without any splitting, whereas the other immediately heavily broadens in some sort of triangular line shape. The field dependence of

M_1 of the two components, shown in Fig. 4, reveals that they differ by a factor of 5. This is attributed to the difference by a factor of 5 in the corresponding average populations of bosons. If there were no hopping of bosons between A and B planes, the B planes should be empty for the range of field such that $\Delta_A < g\mu_B H < \Delta_B$. Although the observed density of boson is finite in the B planes, it is strongly reduced, giving rise to a strong commensurate modulation of \bar{n} along the c axis. According to Ref. 11, the hopping along the c axis of bosons in the condensate is forbidden by the frustration, and can only occur as a correlated jump of a pair. However, this argument does not take into account the IC modulation of the boson density.

In conclusion, this NMR study of the 2D weakly coupled dimers $\text{BaCuSi}_2\text{O}_6$ reveals that the microscopic nature of the BEC in this system is much more complicated than first expected. Two groups of different planes are clearly evidenced, with different intradimer J couplings and a gap ratio of 1.16, in agreement with neutron spectroscopy¹³. Within this self-organized heterostructure, we observed that close to the QCP the density of bosons, which is IC modulated within each plane, is reduced in every second plane along the c axis by a factor of ≈ 5 . New experiments should tell how this peculiar quantum ground state will evolve on further increase of the magnetic field.

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