Low-temperature $^{31}$P NMR study of the two-dimensional frustrated square lattice compound BaCdVO(PO$_4$)$_2$

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Abstract. We report the $^{31}$P NMR spectrum and spin-lattice relaxation rate $1/T_1$ as a function of temperature in the two-dimensional frustrated square lattice compound BaCdVO(PO$_4$)$_2$. The temperature dependence of $1/T_1$ indicates the existence of antiferromagnetic ordering at $T_N \sim 1.05$ K which is also evidenced by the broadening of the NMR spectrum below that temperature. The temperature dependences of $1/T_1$ and $1/T_1T\chi$ just above $T_N$ demonstrate the importance of two-dimensional antiferromagnetic spin correlations for critical fluctuations.

1. Introduction

Geometrical frustration is the source of a variety of fascinating phenomena. Recently much attention has been given to the study of the frustrated $S = \frac{1}{2}$ square lattice (FSL), also known as the $J_1$-$J_2$ model, where the frustration is caused by a next-nearest-neighbor exchange interaction $J_2$, along the diagonal of the square, competing with the nearest-neighbor exchange interaction $J_1$, along the side of the square. The spin Hamiltonian for this model is given by:

$$H = (k_uJ_u)\sum_{ij\neq} S_i \cdot S_j + (k_uJ_u)\sum_{ik\neq} S_i \cdot S_k,$$

(1)

where the first sum is over nearest-neighbor spin pairs and the second is over next-nearest-neighbor spin pairs. From the theoretical studies [1-3], an interesting phase diagram for this model has been proposed which includes three different magnetically ordered phases: ferromagnet [FM, wave vector $Q_{FM} = (0, 0)$], Neel antiferromagnet [NAF, $Q_{NAF} = (\pi, \pi)$] and columnar antiferromagnet [CAF, $Q_{CAF} = (\pi, 0)$ or $(0, \pi)$]. In the classical point of view, first-order phase transition occurs at the phase boundaries. But quantum fluctuations destroy long range magnetic ordering and lead to a disordered ground state at the boundaries. A gapped spin singlet state is proposed for $J_2/J_1 \sim 0.5$, while a gapless nematic state is suggested in the region $-0.4 < J_2/J_1 < -0.7$.

The vanadium phosphate BaCdVO(PO$_4$)$_2$ is considered a prototype of the $J_1$-$J_2$ model. The compound has a layered crystal structure with square-like arrangements of V$^{4+}$ ($3d^1$, $S = \frac{1}{2}$) cations. The exchange interactions $J_1$ and $J_2$ between V$^{4+}$ spins were reported to be $J_1 = -3.6$ K (ferromagnetic) and $J_2 = 3.2$ K (antiferromagnetic) from magnetic susceptibility and magnetization measurements [4]. A long-range antiferromagnetic (AFM) ordering at $T \sim 1$ K is reported from specific heat [4], magnetization [4,5] and muon spin resonance measurements [6]. Based on the ratio
\( J_2 / J_1 \sim -0.9 \), the system is considered to be located close to the phase boundary between CAF and the gapless nematic phase. In this paper, we have carried out \( ^{31}\text{P} \) nuclear magnetic resonance (NMR) measurements at very low temperatures down to 100 mK in order to investigate magnetic properties of BaCdVO(PO\(_4\))\(_2\).

2. Experimental

The polycrystalline samples of BaCdVO(PO\(_4\))\(_2\) were synthesized following the same procedure as has been mentioned in Ref. [4]. The NMR measurements were conducted using pulsed NMR techniques on \( ^{31}\text{P} \) (nuclear spin \( I = 1/2 \) and gyromagnetic ratio \( \gamma = 17.237 \text{ MHz/T} \)) nuclei in the temperature range of 0.1 K \( \leq T \leq 300 \text{ K} \) using a \(^3\text{He}-^4\text{He} \) dilution refrigerator (Kelvinox MX100) installed at Ames Laboratory. There are two inequivalent phosphorus sites (P1 and P2) in the crystal structure. The [VOPO\(_4\)] layers, which extend parallel to the ab-plane, are formed by the corner-sharing V\(^{4+}\)O\(_5\) pyramids with P1O\(_4\) tetrahedra while the other site forms isolated P2O\(_4\) tetrahedra lying between [VOPO\(_4\)] layers. Thus, the P1 site is expected to be strongly coupled and the P2 site weakly coupled to the V\(^{4+}\) spin. The nuclear spin-lattice relaxation rate \( 1/T_1 \) was measured by the single saturation pulse method. The nuclear recovery slightly deviated from a single exponential function so that \( T_1 \) was determined by fitting the recovery curves versus time \( t \) with a stretched exponential function, \( \exp[-(t/T_1)^\alpha] \). The magnetic susceptibility \( \chi(T) \) was measured at two different magnetic fields (1 T and 5 T) using a commercial (Quantum Design) SQUID (Superconducting Quantum Interference Device) magnetometer.

![FIG. 1: (a) \(^{31}\text{P} \) NMR spectra at different temperatures. The vertical line corresponds to the Larmor field \( H_0 \) determined by the reference sample H\(_3\)PO\(_4\). (b) Temperature dependence of the NMR shift \( K \) (\( a, b \) and \( c \) axes) for each P site. The inset shows temperature dependence of \( K_{\text{iso}} \) for the P1 site. The solid line is the fit of \( K_{\text{iso}} \) by Eqs. (2) and (3). (c) \( K-\chi \) plot for all three orientations for each P site.](image-url)
3. Experimental results and discussion

Figure 1(a) shows the $^{31}$P NMR powder spectrum at frequency $f = 70.3$ MHz at various temperatures. The two lines observed are due to the crystallographically inequivalent P sites, P1 and P2, and the spectrum is similar to the one observed in the isostructural Pb$_2$VO(PO$_4$)$_2$ [7]. The narrow line around the Larmor field $H_0$ can be assigned to the P2 site lying between vanadium layers and the other broad line is from the strongly-coupled P1 site. Each line has a characteristic shape of the anisotropic powder pattern. With decreasing temperature, both lines broaden and the broad line shifts to lower magnetic field, while the narrow line shifts to slightly higher magnetic field.

Figure 1(b) shows temperature $T$ dependences of the NMR shifts $K$. For the P1 site, the shifts along the $a$ and $b$ axes are the same within our experimental uncertainty and strongly positive and the shift along the $c$ axis is very small. For the P2 site, there is a relatively small negative shift along the $a$ (and $b$) axis and a small positive shift along the $c$ axis. The NMR shift varies linearly with the spin susceptibility $\chi$, and $K(T)$ can be generally expressed in terms of $\chi(T)$ as

$$K(T) = K_0 + \frac{H_{hf}}{\mu_B N_A} \chi(T),$$

where $K_0$ is the temperature-independent chemical (orbital) shift, $N_A$ is the Avogadro number, $H_{hf}$ is the hyperfine field at the P site in Oe produced by the V$^{4+}$ $S = \frac{1}{2}$ spins and $\chi/N_A$ is expressed in units of $\mu_B/(Oe\cdot spin)$. Shown in Fig. 1(c) is the $K-\chi$ plot with $T$ as the implicit parameter. From the slope of the $K-\chi$ plot, the hyperfine fields at the P sites are estimated to be $H_a = H_b = (3045 \pm 32)$ Oe and $H_c = (149 \pm 21)$ Oe for P1. For P2, $H_a = H_b = -(264 \pm 2)$ and $H_c = (378 \pm 6)$ Oe. The isotropic hyperfine field $H_{iso} = (H_a + H_b + H_c) / 3$ is then $(2080 \pm 28)$ Oe for P1 and $-(50 \pm 3)$ Oe for P2. The isotropic component originates from the isotropic transferred hyperfine interaction (THI) from the V spin moments. The THI between the V and P1 ions is coming from the P(3$s$)-O(2$p$)-V(3$d$) covalent bond in the [VOPO$_4$] layers. The THI at the P2 site evidences that the V 3$d$ spins polarize the 3$s$ electron spins at the P2 site via covalent bonds between the O and Pb atoms, which will be responsible for three-dimensional magnetic interactions in the system. These hyperfine fields are compared with $H_a = (1882 \pm 40)$ Oe, $H_b = (1251 \pm 42)$ Oe and $H_c = -(1642 \pm 55)$ Oe for P1 site in the isostructural Pb$_2$VO(PO$_4$)$_2$ and its anisotropy in $ab$ plane is due to the distortion in the square lattice with lower crystal structure [7]. On the other hand we did not detect any anisotropy in the $ab$ plane in BaCdVO(PO$_4$)$_2$, within our experimental resolution. This indicates that the structural deviation from the square lattice is smaller in BaCdVO(PO$_4$)$_2$ than in Pb$_2$VO(PO$_4$)$_2$.

In order to estimate the exchange couplings $J_1$ and $J_2$, we fitted the temperature $T$ dependence of the isotropic part of the NMR shift for P1 above 15 K by Eq. (2) where $\chi(T)$ is the high-temperature series expansion for the FSL model: [8]

$$\chi(T) = \frac{N_A g^2 \mu_B^2}{k_B T} \sum_n \left( \frac{J_n}{k_B T} \right)^n \sum_m c_{m,n} \left( \frac{J_+}{J_1} \right)^m,$$

where $c_{m,n}$ are the coefficients listed in Table 1 of Ref. [8]. The temperature dependence of $K_{iso}$ is well reproduced with the set of parameters $J_1 = -3.35$ K and $J_2 = 3.53$ K. These values are in good agreement with those reported previously [4].

Figure 2 shows the temperature dependence of the $^{31}$P NMR spectrum below $4$ K at $f = 13.8$ MHz. The P1 NMR line was found to broaden abruptly below $T_N \sim 1.05$ K and shoulder-like features are
observed on either side of the P2 line. The broadening of the lines is due to the presence of the internal field at the P sites. The symmetric broadening indicates staggered moments in the antiferromagnetically ordered state below $T_N$ which is consistent with the CAF ordered state. The inset of Fig. 2 shows the temperature dependence of the line-width ($\Delta H$) for the P2 site, where a sudden increase of $\Delta H$ just below $T_N$ can be observed. Since the $\Delta H$ is proportional to the V$^{4+}$ sublattice magnetization, it is generally possible to estimate a critical exponent for the magnetic transition which depends on the spin and lattice dimensionalities. However we did not attempt to estimate it because of lack of a sufficient number of data points close to $T_N$. In order to obtain an accurate critical exponent, it is obviously needed to measure more data points close to $T_N$. This is currently in progress.

Figure 3(a) shows the temperature dependence of $1/T_1$ measured at the peak position of the narrow line (P2 site). Above 2 K, $1/T_1$ is temperature independent due to the exchange-narrowed hyperfine interactions between the V spin moments in the paramagnetic state. With lowering temperature close to $T_N = 1.05$ K, $1/T_1$ increases and shows a divergent behavior due to critical slowing down of spin fluctuations.

FIG. 2 Temperature dependence of the $^{31}$P NMR spectrum at $f = 13.8$ MHz. The inset shows the temperature dependence of $\Delta H$ for the P2 site.

FIG. 3(a) Temperature dependence of $1/T_1$ for the P2 site at 13.8 MHz. The inset shows the plot of $1/T_1$ vs $\varepsilon = (T - T_N)/T_N$. The solid line is a fit as described in the text. (b) $1/T_1T\chi$ plotted as a function of temperature.
fluctuations. As shown in the inset of Fig. 3(a) the divergent behavior of \(1/T_1\) is approximately fitted by \(1/T_1 \sim e^{-\epsilon}\) with \(\epsilon = (T - T_N)/T_N\) \((T_N = 1.05\ \text{K})\) and \(\nu\) is estimated to be \(\sim 0.7\) which is close to the value of 0.8 expected for a two-dimensional (2D) Heisenberg system [9].

In general, critical fluctuations at the antiferromagnetic wave vector dominate near the antiferromagnetic ordering temperature. To see these effects, it is useful to re-plot the data by changing the vertical axis from \(1/T_1\) to \(1/T_1 \chi\) as shown in Fig. 3(b). \(1/T_1 \chi\) can be expressed in terms of the dynamic susceptibility \(\chi_M(\tilde{q}, \omega_0)\) per mole of electronic spins as [7, 10]

\[
\frac{1}{T_1 \chi} = \frac{2\gamma^2 k_B}{N_A} \sum_q |A(\tilde{q})|^2 \chi_M(\tilde{q}, \omega_0),
\]

where the sum is over the wave vectors \(\tilde{q}\) within the first Brillouin zone, \(A(\tilde{q})\) is the form factor of the hyperfine interactions and \(\chi_M(\tilde{q}, \omega_0)\) is the imaginary part of the dynamic susceptibility at the Larmor frequency \(\omega_0\). A plot of \(1/T_1 \chi\) versus \(T\) shows the relative magnitude of \(\sum_q |A(\tilde{q})|^2 \chi_M(\tilde{q}, \omega_0)\) as compared to the uniform susceptibility \(\chi(0,0)\). For high temperatures above 3 K, \(1/T_1 \chi\) is a constant showing that the temperature dependence of \(\sum_q |A(\tilde{q})|^2 \chi_M(\tilde{q}, \omega_0)\) is equivalent to that of \(\chi(0,0)\). With decrease in temperature, \(1/T_1 \chi\) starts to increase. This implies dominance of \(\sum_q |A(\tilde{q})|^2 \chi_M(\tilde{q}, \omega_0)\) over \(\chi(0,0)\), which is due to a growth of antiferromagnetic correlations. Thus we conclude that 2D antiferromagnetic spin fluctuations play an important role for driving the long range antiferromagnetic ordering in the system. Since the AFM ordered state must be columnar type, it is most likely that the spin correlations originate from the \(\tilde{q} = Q_{CAF}\) component.

Below \(T_N\), \(1/T_1\) decreases sharply and levels off at low temperatures below \(\sim 0.3\ \text{K}\). Similar behavior is observed in the temperature dependence of the muon relaxation rate \(\lambda\) in BaCaVO\(\text{(PO}_4\text{)}_2\) [6]. The constant relaxation rates at low temperatures indicate temperature independent spin fluctuations, which is characteristic of a frustrated spin system with a degenerate ground state.

4. Conclusions

We have carried out \(^{31}\text{P}\) NMR measurements in the 2D frustrated square lattice compound \(\text{BaCdVO(PO}_4\text{)}_2\) down to 0.1 K using a \(^3\text{He-}^4\text{He}\) dilution refrigerator. \(^{31}\text{P}\) spin-lattice relaxation rates \((1/T_1)\) measured at \(H = 0.8\ \text{T}\) are almost independent of temperature above 2 K, show a peak at \(\sim 1.05\ \text{K}\) and become constant below 0.4 K. The temperature dependence of \(1/T_1\) indicates the existence of antiferromagnetic ordering at \(T_N \sim 1.05\ \text{K}\) which is also evidenced by the broadening of the NMR spectrum below that temperature. The temperature dependences of \(1/T_1\) and \(1/T_1 \chi\), just above \(T_N\), provide a prominent evidence of two-dimensional antiferromagnetic spin correlations for critical fluctuations.

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