PHYSICAL REVIEW B **72**, 052409 (2005)

NMR investigation of $BaCu_2V_2O_8$ in alternating-chain and dimer-chain models

C. S. Lue* and B. X. Xie
Department of Physics, National Cheng Kung University, Tainan 70101, Taiwan

(Received 26 April 2005; revised manuscript received 28 June 2005; published 23 August 2005)

^{51}V NMR measurements were performed on the quasi-one-dimensional compound $BaCu_2V_2O_8$. Two ^{51}V NMR lines that are associated with two vanadium crystallographic sites have been resolved. For each site the temperature-dependent NMR shift exhibits a character of low-dimensional magnetism with a broad maximum at $T_{max} \simeq 280$ K. Below T_{max}, the NMR shifts and spin-lattice relaxation rates clearly indicate activated behavior, confirming the spin gap formation in $BaCu_2V_2O_8$. While the alternating-chain model has been proposed to account for the observed spin gap characteristics, our NMR results suggest that the nearly isolated dimer picture could be an alternative scenario for the understanding of the gap feature in this material.

DOI: 10.1103/PhysRevB.72.052409 PACS number(s): 75.10.Pq, 76.60.−k

The understanding of the physics of low-dimensional spin systems has made considerable progress in recent years.[1] For a uniform quasi-one-dimensional chain with half-integer spins, the gapless ground state is expected. However, the alternating-chain interactions can result in the opening of a gap via either frustration due to the next-nearest-neighbor antiferromagnetic exchange or dimerization due to an alternating coupling to nearest neighbors along the chain.[2,3] Several $S=1/2$ chain systems have been reported to possess spin gaps and their characteristics have been interpreted in accordance with these pictures. $(VO)_2P_2O_7$ and $CaCuGe_2O_6$ are materials of this prototype.[4,5]

Recently, an additional member, $BaCu_2V_2O_8$, was added to the list of $S=1/2$ one–dimensional (1D) systems by He and co-workers.[6] $BaCu_2V_2O_8$ crystallizes in a tetragonal structure with the space group I-42d.[7] Taking into account the known oxidation states of O^{2-} and Ba^{2+}, the remaining valences are Cu^{2+} $(S=1/2)$ and nonmagnetic V^{5+}. In this structure, the Cu^{2+} ions have been bridged by oxygen ions, forming the CuO_4 square plaquettes. Vanadium atoms have two nonequivalent crystallographic sites, denoted as V-I and V-II, which are coordinated inside oxygen tetrahedra. The VO_4 tetrahedra with V-I involves an edge-sharing chain with the CuO_4 square plaquettes in the c direction while another VO_4 tetrahedra with V-II separates these chains. Based on the analysis of magnetic susceptibility and heat capacity data,[6] the nature of spin gap was realized as the appearance of two interactions mediated by Cu^{2+} ions within the alternating-chain scenario. One interaction, J_1, is along the Cu-O-V-O-Cu path in the c axis and another, J_2, is the Cu-O-Cu path, which is almost perpendicular to the chain direction. The rather small ratio of $J_2/J_1 \simeq 0.2$ is responsible for the observed large spin gap of about 230 K. In addition to the alternating-chain model, the low-temperature magnetic susceptibility data have been fitted to the dimer model. The fitting result was less satisfactory and He *et al.* thus claimed that $BaCu_2V_2O_8$ should not be classified as a dimerized compound.

It is generally believed that bulk property measurements usually fail to yield reliable estimations if impurity phases and/or defects appear in samples. The nuclear magnetic resonance (NMR) measurement, however, is a local probe that is not sensitive to these extrinsic effects. Hence, in order to elucidate intrinsically magnetic characteristics of $BaCu_2V_2O_8$, we performed a detailed ^{51}V NMR study invoking NMR shifts and spin-lattice relaxation rates on this compound. The experimental results clearly reveal a spin gap in this material. Furthermore, our NMR analysis indicated that the observed spin gap can be well accounted for by the isolated dimer model, contrary to the previous conclusion obtained from the fit of bulk susceptibility.[6]

A polycrystalline $BaCu_2V_2O_8$ compound was synthesized by an ordinary solid-state reaction technique. Briefly, a mixture of an appropriate molar ratio of Ba_2CO_3, CuO, and V_2O_5 was pressed into pellets and heated at 720 °C in an oxygen flow for several days with intermediate grindings. A brown product was obtained. A room-temperature x-ray diffraction taken with Cu $K\alpha$ radiation on the powder sample indicates the expected structure. We thus determined the lattice constants $a=1.273$ nm and $c=0.807$ nm for this compound, close to those reported in the literature.[6–8]

NMR measurements were carried out in a constant field of 70.5 kOe. The specimen was put in a Teflon vial that showed no observable ^{51}V NMR signal.[9] The Knight shift here was referred to the ^{51}V resonance frequency of aqueous $VOCl_3$ in the C_6H_6 solvent. ^{51}V NMR line shapes were obtained from spin-echo fast Fourier transforms using a standard $\pi/2$-τ-π sequence. As given in the inset of Fig. 1, the observed ^{51}V NMR spectrum consists of two features due to the coexistence of two nonequivalent vanadium sites in $BaCu_2V_2O_8$. Both lines gradually merge together with decreasing temperature. Each NMR linewidth is quite narrow, mainly due to dipolar broadening. The width of the spectrum does not change significantly on cooling. These observations confirm the nonmagnetic nature for both V sites, as expected for the nonmagnetic V^{5+} ions. Since the V-I site is associated with the chain path, the corresponding transfer hyperfine field arising from Cu^{2+} ions is larger than that of the V-II site. As a result, a larger NMR shift should be expected for the V-I site. The low-frequency line was thus assigned to the V-II site. Note that the NMR intensity from the V-II site looks stronger due to the combination of satellite lines with the central transition. The values of quadrupole frequency ν_Q, estimated from the shoulders of V-II site and the edges of V-I

1098-0121/2005/72(5)/052409(4)/$23.00

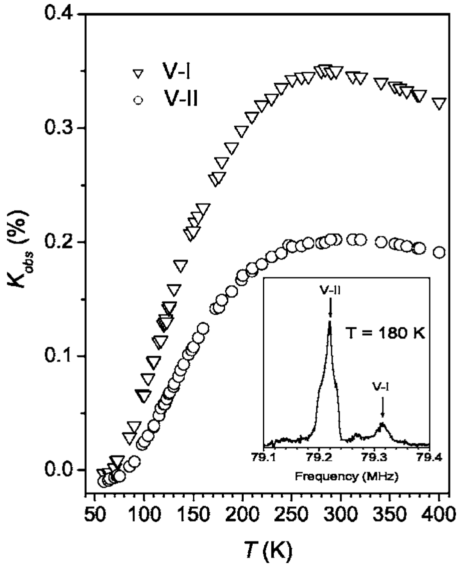

FIG. 1. Temperature dependence of the ^{51}V NMR shifts for both V-I and V-II sites in $BaCu_2V_2O_8$. Inset: the ^{51}V NMR spectrum for $BaCu_2V_2O_8$ measured at 180 K.

site, are 35±5 and 75±10 kHz for V-I and V-II, respectively. Such small ν_Q values indicate that the locations of V atoms are highly symmetric.

In Fig. 1, we displayed the observed temperature-dependent NMR shifts (K_{obs}'s) for both V sites. The shifts were taken at the peak position of each resonance line. Both NMR shifts show a broad maximum near 280 K, consistent with the magnetic susceptibility after subtracting the low-temperature Curie tail arising from paramagnetic impurities.[6] Each K_{obs} can be decomposed into the temperature-independent and temperature-dependent spin parts: $K_{obs} = K_o + K_{spin}(T)$. The first term K_o remains negative with any fit. The tiny negative shift is likely due to the chemical shift, pointing to little contribution arising from the positive orbital shift. Similar observations have been found in other spin gap systems such as $(VO)_2P_2O_7$.[10]

For the temperature-dependent $K_{spin}(T)$, this part vanishes to almost zero at low temperatures, indicative of the gap in the spin excitation spectrum. According to the alternating-chain picture, the spin shift will follow the relation $K_{spin} = (A^{(c)}/\sqrt{T})e^{-\Delta_K^{(c)}/T}$ within the low-temperature limit.[11] Here $\Delta_K^{(c)}$ is the gap energy determined from the NMR shift fitted to the alternating-chain model. Another fitting parameter $A^{(c)}$ is expected to be proportional to the transfer hyperfine coupling constant from Cu^{2+}. As demonstrated in Fig. 2, $K_{spin}(T)$ below 160 K can be fitted successfully to this form. With this fit, we found $\Delta_K^{(c)} = 360 \pm 20$ K and $A^{(c)} = 0.31 \pm 0.03$ K$^{1/2}$ for V-I, and $\Delta_K^{(c)} = 370 \pm 20$ K and $A^{(c)} = 0.18 \pm 0.02$ K$^{1/2}$ for V-II. Note that the extracted $\Delta_K^{(c)}$ values, as listed in Table I, are considerably larger than the 230 K reported by He *et al.*[6] Because the NMR shift measurement is insensitive to extrinsic magnetic impurities, the present result would provide a more reliable estimate. In addition, the ratio of $A^{(c)}(\mathrm{I})/A^{(c)}(\mathrm{II}) = 1.72 \pm 0.03$ is obtained, revealing the relative coupling strength between V-I and V-II with Cu^{2+}. In the inset of Fig. 2, we further plot the shifts for both V sites against magnetic susceptibility deduced from the data of Ref. 6. The slopes yielded the hyperfine fields $H_{hf} = 26.2 \pm 0.3$ and 16.0 ± 0.2 kOe$/\mu_B$ for V-I and V-II, respectively. Thus the ratio of $H_{hf}(\mathrm{I})/H_{hf}(\mathrm{II})$ is 1.64 ± 0.03, consistent with the above analysis.

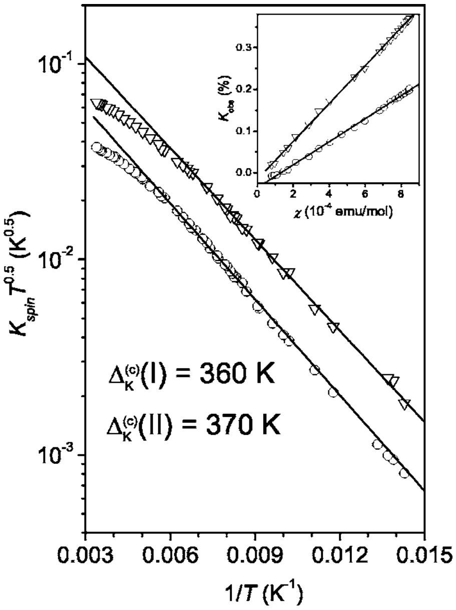

FIG. 2. Plots of $K_{spin}\sqrt{T}$ against $1/T$ for $BaCu_2V_2O_8$. The solid lines indicate the activation law with $\Delta_K^{(c)}$ of 360±20 and 370±20 K for sites I and II, respectively. The inset illustrates the linear relationship between K_{obs} and χ (deduced from Ref. 6).

For one-dimensional $S = 1/2$ spin chain systems, a quantum phase transition from a gapless state into a gapped state can be induced by dimerization. As viewed from the lattice structure of $BaCu_2V_2O_8$ [see Fig. 1(b) in Ref. 6], the spin chain is allowed to be described as an arrangement of spin dimers. Each dimer consists of two CuO_4 square plaquettes and weak interdimer interactions would be responsible for the observed large spin gap. Accordingly, the spin excitation is predominated by the singlet-triplet process and the spin shift is expressed as $K_{spin} = A^{(d)}/T(3 + e^{\Delta_K^{(d)}/T})$.[11] Here the upper index (d) is associated with the dimer model. As shown in Fig. 3, the data can be fitted well in a fairly wide temperature range to this relation, drawn as a solid curve in the figure. In this regard, the spin gap nature may be interpreted in terms of the dimer scenario. The determined $\Delta_K^{(d)}$ values are 460±25 and 470±25 K for V-I and V-II, respectively, as summarized in Table I. Also the ratio of $A^{(d)}(\mathrm{I})/A^{(d)}(\mathrm{II}) = 1.65 \pm 0.03$ is close to $A^{(c)}(\mathrm{I})/A^{(c)}(\mathrm{II}) = 1.72 \pm 0.03$, indicating that this ratio is essentially unaffected by different fits.

TABLE I. Spin gaps for each V crystallographic site, deduced from the NMR shifts and T_1's.

	Δ_K(I)	Δ_K(II)	Δ_R(II)
Alternating chain	360±20 K	370±20 K	440±30 K
Dimer chain	460±25 K	470±25 K	450±30 K

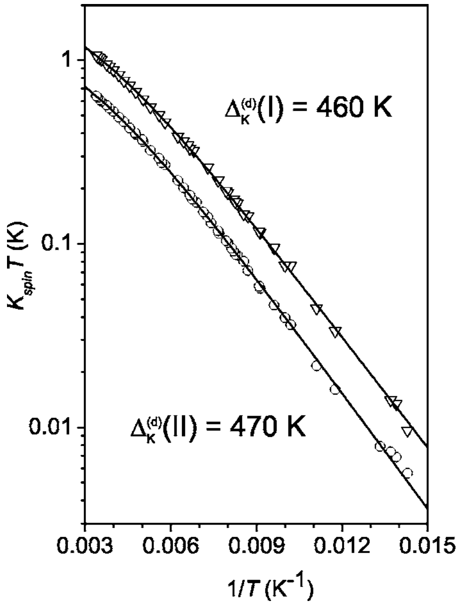

FIG. 3. Plots of $K_{spin}T$ against $1/T$ for $BaCu_2V_2O_8$. The solid curves are fitted to the function described by the dimer model with $\Delta_K^{(d)}$ of 460±25 and 470±25 K for sites I and II, respectively.

To better understand the spin gap characteristics in $BaCu_2V_2O_8$, we performed the spin-lattice relaxation rate $(1/T_1)$ measurement, which is sensitive to the low-energy magnetic excitations. It is known as a suitable probe of spin gap features in the low-dimensional chain compounds. As mentioned, two NMR lines overlap severely at low temperatures, which makes an unambiguous determination of individual $1/T_1$ rather difficult. Here we only measured temperature-dependent $1/T_1$ at the V-II site above 77 K. For each T_1 we recorded the recovery of the ^{51}V spin-echo signal after the application of a long comb of rf pulses. For magnetic relaxation of the central transition with $I=7/2$, the spin-lattice relaxation is expressed as[12]

$$\frac{M(t)}{M(0)} = 1 - 2(0.012e^{-t/T_1} + 0.068e^{-6t/T_1} + 0.206e^{-15t/T_1} + 0.714e^{-28t/T_1}), \tag{1}$$

derived from the initial conditions used in our experiments. T_1 values were thus obtained by fitting to this multiexponential function. A representative recovery curve taken at 85 K is given in the inset of Fig. 4.

The temperature dependence of $1/T_1$ at V-II is displayed in Fig. 4. It is clearly seen that $1/T_1$ exhibits activated behavior at low temperatures. By fitting to the data to an activation law $1/T_1 \propto e^{-\Delta_R^{(c)}/T}$, the energy gap $\Delta_R^{(c)}=440\pm30$ K was extracted. This value, as listed in Table I, is markedly larger than $\Delta_K^{(c)}=370\pm20$ K with the ratio of $\Delta_R^{(c)}/\Delta_K^{(c)} \simeq 1.2$. On the other hand, $1/T_1$ should be fitted to the form $1/T_1 \propto (3+e^{\Delta_R^{(d)}/T})^{-1}$ by analogy with the treatment of NMR shift,[11] based on the dimerized scenario. The fitting result, drawn as a solid curve, is quite satisfactory and yields an energy gap $\Delta_R^{(d)}=450\pm30$ K, good identical with $\Delta_K^{(d)}=470\pm25$ K for the V-II site.

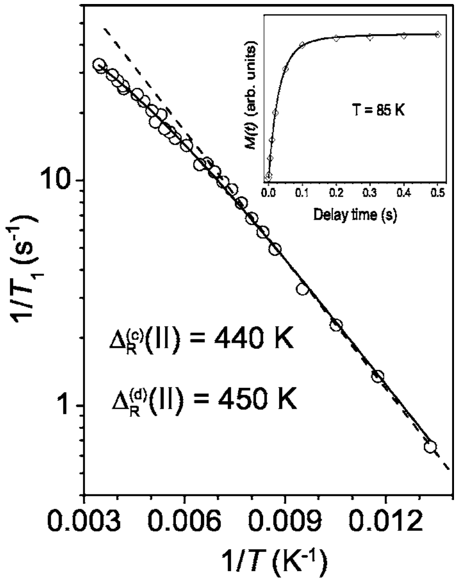

FIG. 4. Inverted-temperature dependence of $1/T_1$ for the V-II site in $BaCu_2V_2O_8$. The dashed line is obtained by fitting to a simple exponential relation. The solid curve is the fitted function based on the dimer model. Inset: a representative recovery curve taken at 85 K. Solid line: a fit to the theoretical recovery behavior from Eq. (1).

Our NMR investigation thus provides a clear evidence for the existence of spin gap in $BaCu_2V_2O_8$. The analyses indicated that either the alternating-chain model or dimer model can be employed to describe the observed gap feature, in spite of the difference in the magnitude of the gap value from different fits. For the latter case, the extracted $\Delta_K^{(d)}$ was found to be close to $\Delta_R^{(d)}$ with the ratio of $\Delta_R^{(d)}/\Delta_K^{(d)} \simeq 1$. Such a result is commonly seen in the dimerized systems.[13,14] This can be considered an interesting feature of the simple singlet-triplet excitation of a dimer. Within the isolated dimer limit, T_{max}, the temperature at which magnetic susceptibility or NMR shift displays a maximum, will appear at around $0.63\Delta_R^{(d)}$.[15] For the present $BaCu_2V_2O_8$, the determined $\Delta_R^{(d)}=450$ K results in $T_{max}=284$ K, in excellent agreement with the observed $T_{max} \simeq$ 280 K. In these regards, $BaCu_2V_2O_8$ might be viewed as a nearly isolated dimer-chain compound.

On the other hand, the ratio of $\Delta_R^{(c)}/\Delta_K^{(c)} \simeq 1.2$ was obtained from the alternating-chain model. This ratio is a bit smaller than those in other gapped quantum spin systems, where larger ratios of $\Delta_R^{(c)}/\Delta_K^{(c)} \simeq 1.4$-2 have been reported.[10,16–18] The spin gap energy extracted from $1/T_1$ exceeding the value determined from NMR shift is generally attributed to additional spin excitation to the relaxation process via hyperfine coupling.[19–22] The reason for the discrepancy between these quantities is not understood at this moment; it is presumably related to the details of spin excitations in $BaCu_2V_2O_8$. Possible magnon excitations involving interbranch and intrabranch transitions, and staggered processes may complicate the observed relaxation rates.[23,24] However, the employment of the alternating-chain picture for the understanding of the spin gap cannot be ruled out from the above argument. According to the alternating-chain model, the numerical result based on the quantum transfer matrix (QTM) method[11] reproduces $T_{max} \simeq 0.6J_1$ for $J_2/J_1=0.1$. This ratio, smaller than $J_2/J_1=0.2$ given from the fit to susceptibility data,[6] should be more appropriate for the present case due to the large spin gap of 370 K found from NMR shifts. In this respect, taking the observed $T_{max} \simeq 280$ K for $BaCu_2V_2O_8$, two interactions $J_1 \simeq 470$ K and $J_2 \simeq 47$ K are thus estimated.

In summary, the NMR investigation of $BaCu_2V_2O_8$ offers an opportunity for the examination of alternating-chain and dimer-chain models on the $S=1/2$ 1D system. Analyses of experimental NMR shifts and spin-lattice relaxation rates imply that both scenarios are suitable for the understanding of the spin gap nature in $BaCu_2V_2O_8$. We further expect that such an undistinguished result in the light of these two pictures on the NMR data would take place for the $S=1/2$ chain material with large spin gap.

We are grateful for the support from the National Science Council of Taiwan under Grant No. NSC-93-2112-M-006-001 (C.S.L).

---

*Email address: cslue@mail.ncku.edu.tw

[1] P. Lemmens, G. Guntherodt, and C. Gros, Phys. Rep. **375**, 1 (2003), and references therein.

[2] T. Barnes, J. Riera, and D. A. Tennant, Phys. Rev. B **59**, 11384 (1999).

[3] Kai P. Schmidt, Christian Knetter, and Gotz S. Uhrig, Phys. Rev. B **69**, 104417 (2004).

[4] T. Barnes and J. Riera, Phys. Rev. B **50**, 6817 (1994).

[5] A. Zheludev, G. Shirane, Y. Sasago, M. Hase, and K. Uchinokura, Phys. Rev. B **53**, 11642 (1996).

[6] Z. He, T. Kyomen, and M. Itoh, Phys. Rev. B **69**, 220407 (2004).

[7] R. Vogt and Hk. Muller-Buschbaum, Z. Anorg. Allg. Chem. **591**, 167 (1990).

[8] Z. He, T. Kyomen, and M. Itoh, J. Cryst. Growth **274**, 486 (2005).

[9] C. S. Lue and J. H. Ross, Jr., Phys. Rev. B **60**, 8533 (1999).

[10] J. Kikuchi, K. Motoya, T. Yamauchi, and Y. Ueda, Phys. Rev. B **60**, 6731 (1999).

[11] M. Troyer, H. Tsunetsugu, and D. Wurtz, Phys. Rev. B **50**, 13515 (1994).

[12] W. W. Simmons, W. J. O'Sullivan, and W. A. Robinson, Phys. Rev. **127**, 1168 (1962).

[13] Y. Furukawa, A. Iwai, K. Kumagai, and A. Yakubovsky, J. Phys. Soc. Jpn. **65**, 2393 (1996).

[14] M. Isobe and Y. Ueda, J. Phys. Soc. Jpn. **65**, 3142 (1996).

[15] Y. Itoh and H. Yasuoka, J. Phys. Soc. Jpn. **66**, 334 (1997).

[16] M. Azuma, Z. Hiroi, M. Takano, K. Ishida, and Y. Kitaoka, Phys. Rev. Lett. **73**, 3463 (1994).

[17] T. Shimizu, D. E. MacLaughlin, P. C. Hammel, J. D. Thompson, and S.-W. Cheong, Phys. Rev. B **52**, R9835 (1995).

[18] M. Takigawa, T. Asano, Y. Ajiro, M. Mekata, and Y. J. Uemura, Phys. Rev. Lett. **76**, 2173 (1996).

[19] J. Kishine and H. Fukuyama, J. Phys. Soc. Jpn. **66** , 26 (1997).

[20] S. Sachdev and K. Damle, Phys. Rev. Lett. **78**, 943 (1997).

[21] G. Bouzerar, A. P. Kampf, and G. I. Japaridze, Phys. Rev. B **58**, 3117 (1998).

[22] K. P. Schmidt, C. Knetter, and G. S. Uhrig, Phys. Rev. B **69**, 104417 (2004).

[23] G. Chaboussant, M.-H. Julien, Y. Fagot-Revurat, L. P. Levy, C. Berthier, M. Horvatic, and O. Piovesana, Phys. Rev. Lett. **79**, 925 (1997).

[24] G. Chaboussant, Y. Fagot-Revurat, M.-H. Julien, M. E. Hanson, C. Berthier, M. Horvatic, L. P. Levy, and O. Piovesana, Phys. Rev. Lett. **80**, 2713 (1998).