Mixed valency and charge ordering in α'-NaV_2O_5

Tetsuo Ohama,* Hiroshi Yasuoka, Masahiko Isobe, and Yutaka Ueda
Institute for Solid State Physics, University of Tokyo, Roppongi, Minato-ku, Tokyo 106-8666, Japan
(Received 28 July 1998)

We report ^{51}V NMR measurements in α'-NaV_2O_5, which has been considered as a spin-Peierls (SP) system. Above the transition temperature T_C, only one set of V sites was observed in the NMR spectra, indicating that all the V sites are in a uniform electronic state with the average oxidation of $V^{4.5+}$. Below T_C, there appear two inequivalent sets of V sites assigned to V^{4+} and V^{5+} states. This result indicates that the phase transition in α'-NaV_2O_5 is not a conventional SP transition but a charge ordering. Below T_C, $1/T_1$ at the V^{4+} sites has an activated T dependence, confirming a spin-singlet ground state with the excitation gap $\sim$108 K. [S0163-1829(99)11705-3]

A spin-Peierls (SP) transition is an example of fascinating phenomena observed in quantum spin systems. The discovery of the SP transition in an inorganic system $CuGeO_3$ (Ref. 1) has renewed interest in this phenomenon. Recently, the SP transition in α'-NaV_2O_5 was strongly suggested by magnetic susceptibility measurements.[2] A previous structural study of this compound at room temperature[3] reported that there are two inequivalent sets of V sites assigned to $V^{4+}[(3d)^1]$ and $V^{5+}[(3d)^0]$, respectively. Each set of V sites has an environment of a corner-sharing VO_5 pyramid, and the V^{4+} sites with one d electron carrying a spin 1/2 form linear chains along the b axis well separated by V^{5+} chains. Actually, above the transition temperature ($T_C \sim 34$ K), the magnetic susceptibility satisfactorily fits the numerical calculation for the spin-1/2 nearest-neighbor Heisenberg chain[4] with $J \sim 560$ K.[2] Although a structural phase transition was indeed observed by x-ray diffraction,[5] ^{23}Na NMR,[6] and Raman scattering[7] measurements, the observed superlattice reflection in the x-ray diffraction could not be understood as a consequence of simple dimerization in isolated linear chains and many other experimental observations question whether this material is an ideal one-dimensional system exhibiting a conventional SP transition. An inelastic neutron scattering measurement[8] observed spin correlation along the a axis in a period of $a/3$ below T_C, implying a charge distribution different from the room temperature structure. Furthermore, two adjacent phase transitions were observed around T_C in a thermal expansion measurement.[9] A recent crystal structure analysis, interestingly, indicates that there is only one set of V sites.[10,11] At present the nature of the phase transition in α'-NaV_2O_5 is poorly understood.

In this article, we report ^{51}V NMR measurements with a single-crystalline sample as well as a powder sample. Below T_C, two inequivalent sets of V sites were observed in the NMR spectra; these V sites have hyperfine couplings consistent with V^{4+} and V^{5+} ions, respectively. Above T_C, only one set of magnetic (meaning having d electrons on site) V sites was observed, indicating that all V sites are in a uniform electronic state with the average oxidation state of $V^{4.5+}$. Below T_C, the nuclear spin-lattice relaxation time T_1 at the V^{4+} sites shows an activated temperature dependence with a spin gap of $\sim$108 K. Our results demonstrate that the phase transition at T_C in α'-NaV_2O_5 is a charge ordering into an electron configuration with a spin excitation gap.

A single-crystalline sample of 140 mg (sample S) and a polycrystalline sample (sample P) were used in this study. The single-crystal growth is described elsewhere.[12] Sample P is the magnetically aligned sample which is the same as used in previous NMR measurements.[6,13] The alignment direction is such that the alignment field (H_{al}) is distributed in the ab plane and is mainly along the b axis.

Figure 1 shows spin-echo spectra below T_C measured at 20 K with sample P. Singularities in the spectra for the external field $H \| H_{al}$ (a) and $H \perp H_{al}$ with rf pulse separation τ of 130 μs (b) are assigned to a set of V sites (site A) with nuclear quadrupolar frequency $\nu_Q \sim 0.40$ MHz and quadrupolar asymmetry parameter $\eta \sim 0.48$. The x, y, and z axes are taken as the principal axes of the electrical field gradient tensor $V_{\alpha\beta}$ so as to give $|V_{yy}| \leq |V_{xx}| \leq |V_{zz}|$. In the spectrum for $H \perp H_{al}$ with τ of 13 μs (c), a spin-echo signal assigned

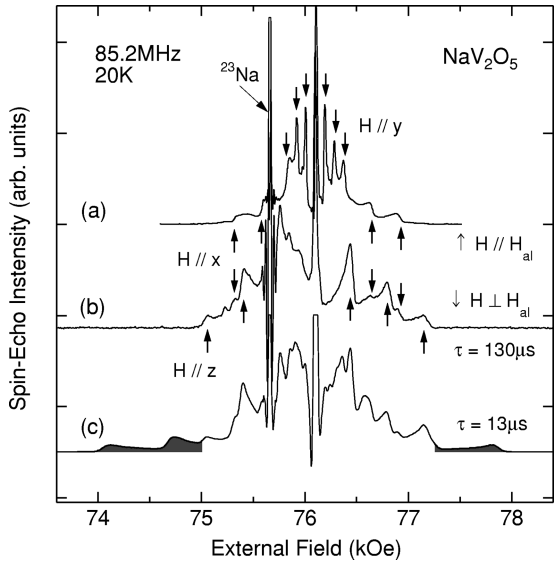

FIG. 1. NMR spectra on sample P measured at 20 K: (a) $H \| H_{al}$, (b) $H \perp H_{al}$ with τ of 130 μs, and (c) $H \perp H_{al}$ with τ of 13 μs. Singularities assigned to site A are shown by arrows. Hatched areas are assigned to site B.

 ©1999 The American Physical Society

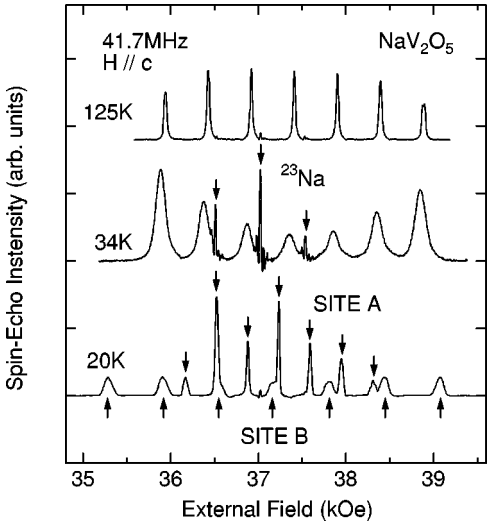

FIG. 2. NMR spectra for $H\|c$ on sample S.

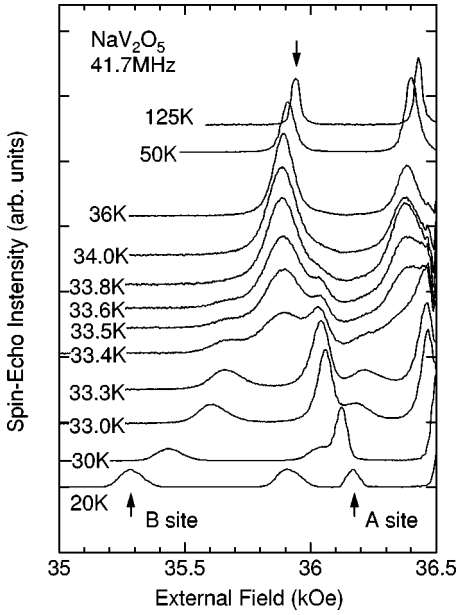

FIG. 3. Temperature dependence of the NMR spectrum for $H\|c$ around T_C on sample S. Third satellite lines are shown by arrows.

to another set of V sites (site B) was clearly observed. Site B has $\nu_Q \sim 0.71$ MHz and a spin-echo decay rate much shorter than site A.

To understand the origin of these two sets of V sites below T_C, we examined the evolution of the spectrum with temperature using a single-crystalline sample. Spin-echo spectra for $H\|a$ and c were measured at several resonance frequencies between 41 and 122 MHz with sample S. No intrinsic frequency dependence was observed. In comparison of the spectra on samples S and P taken at the same resonance frequency, it was found that the a and c axes are indistinguishable from the x and z axes, respectively. Above T_C, the y axis is identical to the b axis since the ac plane is a mirror plane. Thus we can reasonably neglect the difference between the principal axes of $V_{\alpha\beta}$ and the crystalline axes both above and below T_C.

Spin-echo spectra for $H\|c$ measured at 41.7 MHz are shown in Fig. 2. In the spectrum at 20 K below T_C, two sets of V sites are definitely assigned. Above T_C, by contrast, we could observe neither spin-echo nor free-induction decay other than signals assigned to a set of V sites, which sites are magnetic as revealed by a NMR shift measurement.[13] Since nonmagnetic V^{5+} sites, in general, have a much longer spin-echo decay rate than magnetic V sites, there is no reason why the NMR signal from the V^{5+} sites cannot be observed in α'-NaV_2O_5. It is thus concluded that only magnetic V sites exist above T_C, contrary to an electron configuration with equal numbers of V^{4+} and V^{5+} sites, believed so far. Our observation of only one set of magnetic V sites cannot rule out the existence of another set of magnetic sites which are invisible in the NMR spectrum. As we will show later, however, this situation is unlikely. Thus the V sites are in the average oxidation state of $V^{4.5+}$.

The temperature dependence of the spectra near the low-field third satellite line is shown in Fig. 3. The satellite line observed at high temperatures disappears below 33.4 K, while a pair of satellite lines, which correspond to sites A and B, appears below about 34.0 K. These high- and low-temperature lines coexist in this narrow temperature range in sample P. Since the disappearance of the high-temperature line is steep, we believe that this complicated behavior of the phase transition is not due to the distribution of T_C but intrinsic.

We measured the NMR shift for $H\|a$ and c between 10 and 300 K with sample S. The result above T_C agrees with the previous measurement with sample P.[13] The temperature dependence of the shift below 100 K is shown in Fig. 4. The shifts for $H\|b$ at site A measured with sample P are also shown. The difference in the shifts between sites A and B is significant. At magnetic sites in spin-gapped systems, the residual shift at low temperatures, K_{res}, is usually of orbital origin. At site B, $K_{res} \sim 0.10\%$ and 0.27% along the a and c axes, respectively, are similar to the orbital shift at the V^{4+} sites in CaV_2O_5 (Ref. 14) and CaV_4O_9 (Ref. 15), which compounds have a similar VO_5 structure to α'-NaV_2O_5. However, K_{res} at site A seems significantly smaller than at site B, suggesting that the fraction of d electrons at site A is small.

The NMR shifts are plotted against the anisotropic magnetic susceptibility[12] in Fig. 5. Notice that the formula unit

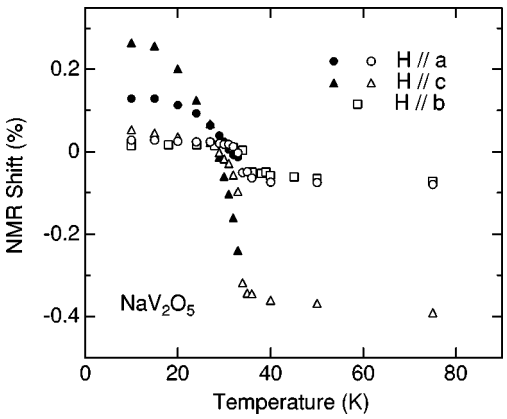

FIG. 4. Temperature dependence of the NMR shift for $H\|a$ and c on sample S and for $H\|b$ at site A on sample P is shown: open symbols for site A and solid symbols for site B below T_C.

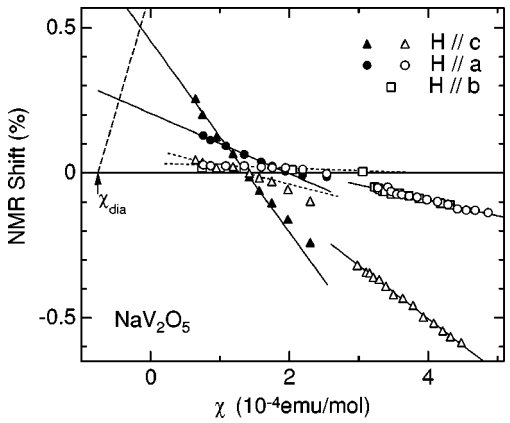

FIG. 5. NMR shifts are plotted against the magnetic susceptibilities: open symbols for site A and solid symbols for site B below T_C. The dashed line shows the orbital hyperfine coupling for a free V^{4+} ion.

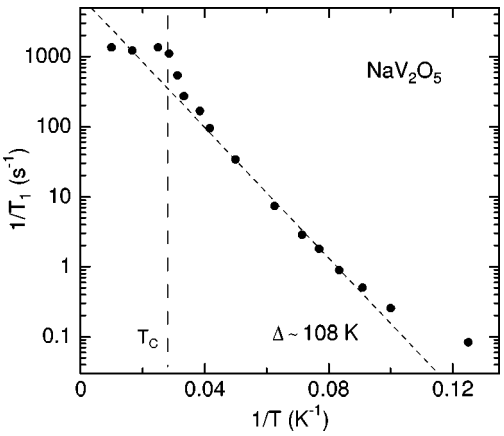

FIG. 6. Temperature dependence of T_1 at site B on sample P. The dashed line shows an activated temperature dependence with Δ of 108 K.

contains two V atoms. The slants of this K-χ plot give the spin part of the hyperfine coupling; the deduced couplings are given in Table I, where the coupling is defined as the hyperfine field for a magnetic moment of $1\mu_B$ per d electron. There is a clear contrast between sites A and B also in the hyperfine coupling. The spin hyperfine coupling, in general, has contributions from the isotropic core-polarization and anisotropic spin dipolar parts.[16] The isotropic part A_{iso} at V^{4+} sites is often of the order of ~ -100 kOe/μ_B [for example, -85 kOe/μ_B in VO_2 (Ref. 17) and -113 kOe/μ_B in CaV_2O_5 (Ref. 18)]. The dipolar part for a pure d_ϵ orbital is axially anisotropic. It is estimated[13] as $A_\parallel = -(4/7)\mu_B\langle r^{-3}\rangle \sim -132$ kOe/μ_B for H along the fourfold rotation axis of a d_ϵ orbital and $A_\perp = +(2/7)\mu_B\langle r^{-3}\rangle \sim +66$ kOe/μ_B for H perpendicular to the rotation axis using the free-ion value of $\langle r^{-3}\rangle$,[16] giving $A_{ax} \equiv (2/3)(A_\parallel - A_\perp) \sim -132$ kOe/μ_B. The deduced coupling for site B is consistent with an estimate for V^{4+} with the d_{xy} orbital occupied, with $A_{iso} \sim -100$ kOe/μ_B and $A_{ax} \sim -84$ kOe/μ_B. The reduction of A_{ax} is reasonably ascribed to the mixing of the other orbital states and the expansion of the d orbital. On the other hand, the couplings at site A are much smaller than at site B and above T_C. These results indicate that d electrons, which occupy all V sites equivalently above T_C, almost localize at site B below T_C. It is also found that the d_{xy} character of the d orbital above T_C (Ref. 13) remains at site B below T_C. This agrees with the electron spin resonance (ESR) result of no significant change in the g values at T_C.[19] This charge ordering does not significantly modify the orbital character. The coupling for $H\|c$ at site A is significantly stronger than the dipolar coupling ~ 1 kOe/μ_B; this is possibly due to the fact that a small fraction of a d electron exists at site A.

TABLE I. Hyperfine couplings in kOe/μ_B in α'-NaV_2O_5.

	$H\|a$	$H\|b$	$H\|c$
Below T_C			
Site A	-5	-1	-34
Site B	-58		-184
Above T_C	-30	-20 [a]	-103

[a]Reference 13.

To confirm the spin-singlet ground state, we measured the temperature dependence of $1/T_1$ at site B with sample P, as shown in Fig. 6. We measured T_1 at one of the third satellite lines for $H\|c$ (~ 78 kOe), employing the inversion recovery method except near T_C. Since the measured recovery of nuclear magnetization deviates from that expected for one inversion pulse between about 25 K and T_C, we employed the comb-pulse method and determined T_1 as the longer component in fitting the recovery by the sum of two exponential components in this temperature range. The deduced $1/T_1$ decreases rapidly with decreasing temperature, demonstrating the spin-singlet ground state with a spin gap. We fit the T_1 below 25 K by an activated temperature dependence $1/T_1 \propto \exp(-\Delta/T)$ and obtained the spin gap $\Delta \sim 108$ K. This gap agrees with that determined from the susceptibility, ~ 98 K.[6] The deviation at low temperatures from the activated temperature dependence is possibly due to an impurity relaxation.

It has been pointed out[13] that the residual susceptibility χ_{res} below T_C is remarkably larger than the values of χ_{orb} estimated from the g values and determined in the K-χ plot above T_C. A similar disagreement between χ_{res} and χ_{orb} below T_C is found in the K-χ plot for site B. If both χ_{res} and K_{res} originated in the orbital susceptibility, the ratio $K_{res}/(\chi_{res} - \chi_{dia})$ is given by the orbital hyperfine coupling. However, the observed values 48 kOe/μ_B for $H\|a$ and 106 kOe/μ_B for $H\|c$ are considerably smaller than 461 kOe/μ_B estimated from the free ion value of $\langle r^{-3}\rangle$[16] and the diamagnetic susceptibility $\sim -7.6\times 10^{-5}$ emu/mol.[20] It is clear that this anomalous χ_{res} cannot originate in the spin susceptibility for the spin-singlet ground state. Its origin is still an open question.

We return now to the possibility of the existence of other magnetic V sites. Above T_C, $A_{iso} \sim -51$ kOe/μ_B is almost half as large as at site B. In a rough estimate, the V sites are occupied by 0.5 d electrons on average above T_C. Since there are 0.5 d electrons per V site in the composition of α'-NaV_2O_5, this suggests the absence of other magnetic V sites. If there are invisible magnetic V sites above T_C, we fail to observe them due to the large spin-echo decay rate governed by a fast T_1 process. We expect $1/T_1$ at such invisible sites to be more than about 20 ms^{-1} according to the limitation of

our spectrometer. On the other hand, $1/T_1$ at the observed sites is $\sim 1.4\ \mathrm{ms}^{-1}$ for $H \| c$ ($1/T_1$ is the lowest for this direction) between 50 and 150 K. Since there is only one *d* electron in a unit cell, the unique spin degree of freedom determines $1/T_1$ at all the nuclear sites, and thus the hyperfine coupling is responsible for the nuclear site dependence of $1/T_1$. Then the coupling at the invisible sites is at least about 4 times larger than the observed sites: $A_{iso} \sim -200\ \mathrm{kOe}/\mu_B$. This value is unreasonable for V sites with less than one *d* electrons. Furthermore, a previous continuous-wave NMR measurement observed only one set of magnetic ^{51}V sites with a large negative shift between 77 and 300 K.[21] These observations show the absence of other magnetic V sites.

The result that all V sites are equivalent above T_C means that α'-NaV_2O_5 has a ladder structure along the *b* axis, very similar to that of CaV_2O_5.[22] Since its electric conductivity is insulating[23] in spite of the oxidation state of $V^{4.5+}$, the *d* electron should localize in a small cluster and be shared by several V ions. The V ions have three types of neighboring V ions. One is the neighbors along the leg of the ladders, and another is on the neighboring ladders, forming a zigzag chain. Since electron transfer between these neighboring V ions would cause one-dimensional conduction, these V ions probably do not share a *d* electron. The other type of neighbors is on the opposite end of the rung of a ladder. Since electron transfer between two V ions on the rung opposite is compatible with the insulating behavior, it is most probable that the *d* electron delocalizes in a dimer of two adjacent VO_5 pyramids on a rung.

In summary, in the ^{51}V NMR spectrum measurement, only one set of V sites is observed above T_C, while two inequivalent sets of V sites which are consistently assigned to V^{4+} and V^{5+} states were observed below T_C. The V sites above T_C are in a uniform electronic state with the average oxidation state of $V^{4.5+}$. This result indicates that the phase transition in α'-NaV_2O_5 is not a conventional SP transition but a charge ordering into a geometrical configuration of charge with a spin gap. The temperature dependence of T_1 at the V^{4+} sites below T_C is consistent with a spin-singlet ground state with a spin gap of ~ 108 K.

We acknowledge Y. Itoh and T. Yosihama for stimulating discussions, and M. Takigawa for helpful discussions and a critical reading of manuscript. This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas from the Ministry of Education, Science, Sports and Culture.

*Present address: Department of Physics, Faculty of Science, Chiba University, Chiba 263-8522, Japan.

[1] M. Hase, I. Terasaki, and K. Uchinokura, Phys. Rev. Lett. **70**, 3651 (1993).
[2] M. Isobe and Y. Ueda, J. Phys. Soc. Jpn. **65**, 1178 (1996).
[3] A. Carpy and J. Galy, Acta Crystallogr. B **31**, 1481 (1975).
[4] J. C. Bonner and M. E. Fisher, Phys. Rev. **135**, A640 (1964).
[5] Y. Fujii, H. Nakao, T. Yosihama, M. Nishi, K. Nakajima, K. Kakurai, M. Isobe, Y. Ueda, and H. Sawa, J. Phys. Soc. Jpn. **66**, 326 (1997).
[6] T. Ohama, M. Isobe, H. Yasuoka, and Y. Ueda, J. Phys. Soc. Jpn. **66**, 545 (1997).
[7] M. Weiden, R. Hauptmann, C. Geibel, F. Steglich, M. Fischer, P. Lemmens, and G. Güntherodt, Z. Phys. B **103**, 1 (1997).
[8] T. Yoshihama, M. Nishi, K. Kakajima, K. Kakurai, Y. Fujii, M. Isobe, C. Kagami, and Y. Ueda, J. Phys. Soc. Jpn. **67**, 744 (1998).
[9] M. Köppen, D. Pankert, R. Hauptmann, M. Lang, M. Weiden, C. Geibel, and F. Steglich, Phys. Rev. B **57**, 8466 (1998).
[10] H. G. von Schnering, Yu. Grin, M. Kaupp, M. Somer, R. K. Kremer, O. Jepsen, T. Chatterji, and M. Weiden, Z. Kristallogr. **213**, 246 (1998).
[11] H. Smolinski, C. Gros, W. Weber, U. Peuchert, G. Roth, M. Weiden, and C. Geibel, Phys. Rev. Lett. **80**, 5164 (1998).
[12] M. Isobe, C. Kagami, and Y. Ueda, J. Cryst. Growth **181**, 314 (1997).
[13] T. Ohama, H. Yasuoka, M. Isobe, and Y. Ueda, J. Phys. Soc. Jpn. **66**, 3008 (1997).
[14] H. Iwase, M. Isobe, Y. Ueda, and H. Yasuoka, J. Phys. Soc. Jpn. **65**, 2397 (1996).
[15] T. Ohama, H. Yasuoka, M. Isobe, and Y. Ueda, J. Phys. Soc. Jpn. **66**, 23 (1997).
[16] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Oxford, London, 1970).
[17] K. Takanashi, H. Yasuoka, Y. Ueda, and K. Kosuge, J. Phys. Soc. Jpn. **52**, 3953 (1983).
[18] T. Ohama, H. Yasuoka, M. Isobe, and Y. Ueda (unpublished).
[19] A. N. Vasil'ev *et al.*, Phys. Rev. B **56**, 5065 (1997).
[20] R. R. Gupta, in *Diamagnetic Susceptibility*, edited by O. Madelung, Landolt-Bornstein, New Series, Group II, Vol. 16, (Springer, Berlin, 1986).
[21] K. Ogawa, M. Onoda, and H. Nagasawa, J. Phys. Soc. Jpn. **55**, 2129 (1986). They observed another ^{51}V site with almost zero shift. This may originate in a secondary phase or ^{23}Na satellite lines.
[22] J. C. Bouloux and J. Galy, J. Solid State Chem. **16**, 385 (1976).
[23] M. Isobe and Y. Ueda, J. Alloys Compds. **262-263**, 180 (1997).