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Charge ordering in NaV_6O_{15} : ^{51}V NMR in a single crystal

Masayuki Itoh[a] Nobuyuki Akimoto[b] Hiroyuki Yamada[c] Masahiko Isobe[c] and Yutaka Ueda[c]

[a] Department of Physics, Faculty of Science, Chiba University,
1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

[b] Graduate School of Science and Technology, Chiba University,
1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

[c] Institute for Solid State Physics, University of Tokyo,
7-22-1 Roppongi, Minato-ku, Tokyo 106-8666, Japan

We have made NMR measurements on a sample of single crystals to study a charge ordering in NaV_6O_{15}, a mixed valence oxide of V^{4+} and V^{5+}. Our NMR results clearly show that the charge ordering takes place at T_{co}=130 K in NaV_6O_{15}.

Quantum spin systems with a characteristic low-dimensional structure have attracted much attention from both experimental and theoretical aspects. The phase transition in α'-NaV_2O_5 first discussed as the spin-Peierls transition [1] is considered to be a charge ordering transition in a quarter-filled spin-ladder system. Theoretically the intersite Coulomb interaction was pointed out to play an important role in the formation of the charge ordering in NaV_2O_5 [2]. We investigated various vanadium oxides to understand phenomena of the charge ordering. In vanadium bronzes $A_xV_2O_5$ (A = alkali, alkaline earth and metals) which contain NaV_2O_5, it is known that there are several phases with structual, magnetic and electric properties different from each other. Recently we found phenomena which may come from the charge ordering in $Na_{1/3}V_2O_5$ (NaV_6O_{15}), a mixed valence oxide of V^{4+} and V^{5+}, with the β structure where there are three V sites, V1, V2, and V3 [3, 4]. In this paper we have made ^{51}V NMR experiments using a sample of single crystals to study the charge ordering in NaV_6O_{15}.

Small single crystals of NaV_6O_{15} were grown by a self flux method as was described in Ref. [3]. NMR experiments were made for a sample of the single crystals stacked parallel to the b-axis.

We observed a drastic change in the ^{51}V NMR spectrum at T_{co}=130 K. Figure 1 shows the NMR spectra taken at 40, 80 and 160 K with an external filed H parallel to the b-axis. Above T_{co} we observed two sets of ^{51}V NMR spectrum as are denoted by S1 and S2 in the spectrum at 160 K. Each spectrum is well explained by taking account of the electric quadrupole effect. However below T_{co} three sets of NMR spectrum were observed as is seen in the spectrum at 80 K. The S2 spectrum is split into two spectra denoted by $S2_a$' and $S2_b$'. With further decreasing temperature T we observed an additional spectrum (S3') with a short nuclear spin-spin relaxation time. Thus we observed the four ^{51}V NMR spectra below T_{co}. This change in the NMR spectrum indicates that the charge ordering from a mixed valence state to a charge-ordering state takes place at T_{co}.

From these NMR spectra, we determined the ^{51}V Knight shift parallel to the b-axis, K_b. Figure 2 shows the T dependence of K_b for each spectrum. A jump of K_b is clearly seen at T_{co}. Also it should be noted that the S1', $S2_a$' and $S2_b$' shifts gradually increase with decreasing T below T_{co}. This means that the spin susceptibilities of S1', $S2_a$' and $S2_b$' decrease with decreasing T. On the other hand, the S3' shift decreases with decreasing T. That is, the spin susceptibility of S3' increases with decreasing T, obeying the magnetic susceptibility. Thus the S3' spectrum is concluded to come from the magnetic V^{4+} site.

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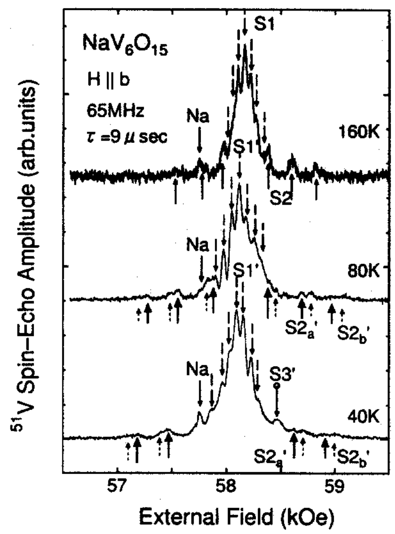

Figure 1. NMR spectra taken at 40, 80 and 160 K with the external filed parallel to the b-axis in NaV_6O_{15}. The arrows in each ^{51}V NMR spectrum (S1, S2, S1', $S2_a$', $S2_b$' and S3') represent central and/or satellite transitions due to the electric quadrupole effect.

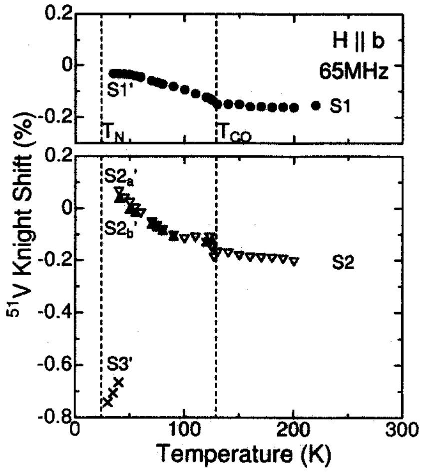

Figure 2. Temperature dependence of the ^{51}V Knight shifts parallel to the b-axis in NaV_6O_{15}.

We also observed a drastic change in the nuclear quadrupole frequency of each V site accompanied by the chare ordering at T_{co}.

In the antiferromagnetic (AF) state below T_N=24 K, we observed ^{51}V antiferromagnetic nuclear resonance (AFNR) in zero external field. At 1.5 K, the AFNR spectra were observed at 0.1, 17.9, 30.3 and 81.0 MHz, corresponding to the four paramagnetic NMR spectra. The AFNR spectra at 0.1 and 81.0 MHz are reasonably concluded to come from the nonmagnetic V^{5+} (S1') and the magnetic V^{4+} (S3') sites, respectively. On the other hand, the spectra at 17.9 and 30.3 MHz are considered to be due to the V^{5+} sites ($S2_a$' and $S2_b$') with a transferred hyperfine field from the V^{4+} site. Thus these AFNR spectra clearly show the presence of the charge ordering below T_{co}. We also found from the analysis of the S1' NMR spectrum that the nonmagnetic V^{5+} site is the V3 site. Therefore the magnetic V^{4+} site should be located at the V1 or V2 site. One possible model of the charge ordering structure is a zigzag or single-chain structure of V^{4+} located at the V2 site. Another is a single-chain structure located at the V1 site.

In conclusion we found from the present ^{51}V NMR measurements that a charge ordering takes place at 130 K in NaV_6O_{15}.

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