Electronic States of Half-Metallic Chromium Oxides Probed by $^{53}$Cr NMR

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Abstract. We have performed $^{53}$Cr NMR measurements to investigate local electronic states of $K_2Cr_8O_{16}$ and $CrO_2$ which are ferromagnetic half-metals with high valent chromium ions. In the ferromagnetic metallic phases of both oxides, we observed at least two $^{53}$Cr NMR spectra which are inconsistent with crystallographically inequivalent one chromium site on a tetragonal lattice, the hollandite structure (symmetry $I4/m$) of $K_2Cr_8O_{16}$ and the rutile structure ($P4_2/nnm$) of $CrO_2$. The origin of this anomalous electronic state may be associated with an electronic phase separation in double exchange systems with the mixed valence.

1. Introduction

In 3d transition metal oxides, a double exchange interaction is one of the origins for itinerant ferromagnetism [1]. The interaction is entangled with the charge, orbital and spin degrees of freedom of the 3d electrons, resulting in complex phase diagrams and several fascinating phenomena such as colossal magnetoresistance and electronic phase separation in Mn oxides [2, 3].

Recently a quasi-one-dimensional chromium oxide $K_2Cr_8O_{16}$ with the hollandite structure as shown in Fig. 1 (a) has attracted much attention as a new ferromagnetic half-metal [4]. It undergoes a ferromagnetic transition at $T_C = 180$ K and exhibits a metal-insulator transition (MIT) at $T_{MI} = 95$ K in the ferromagnetic state. From a theoretical point of view [5, 6], the electronic state of $K_2Cr_8O_{16}$ is similar to that of another ferromagnetic half-metal $CrO_2$ with $T_C = 395$ K and the rutile structure as shown in Fig. 1 (b). These oxides are considered to have a degenerate orbital $d_{yz,zx}$, which forms a broad band due to the strong hybridization with oxygen 2p orbitals, and a nondegenerate orbital $d_{xy}$ which forms a relatively narrow band, resulting in the ferromagnetism due to the double exchange mechanism as presented in Figs. 1 (c) and (d). The average 3d electron number is 2.25 in $K_2Cr_8O_{16}$, whereas it is formally two in $CrO_2$ but the electronic state may be in a mixed-valence state due to the self-doping from oxygen ions to chromium ions in the negative charge transfer region [5]. The electron correlation and the possible competition of magnetic interactions are expected to result in an anomalous electronic state in the double exchange systems such as $K_2Cr_8O_{16}$ and $CrO_2$.

In this study, we have performed $^{53}$Cr NMR measurements to investigate the local electronic states of the ferromagnetic half-metals $K_2Cr_8O_{16}$ and $CrO_2$. NMR spectra coming from more
than two chromium sites with electronic states different from each other are observed in the ferromagnetic metallic phase of K$_2$Cr$_8$O$_{16}$ and CrO$_2$. This is inconsistent with one chromium site on a tetragonal lattice, the hollandite structure of K$_2$Cr$_8$O$_{16}$ and the rutile structure of CrO$_2$. This coexistence may be related to an electronic phase separation as discussed in the Mn oxides.

2. Experimental procedure
A sintered powder sample of K$_2$Cr$_8$O$_{16}$ used in the present NMR measurements was prepared by a solid state reaction of a mixture with the ratio K$_2$Cr$_2$O$_7$ : Cr$_2$O$_3$ = 1 : 3 under 6.7 GPa at 1273 K for 1 h [4], whereas a commercial polycrystalline sample of CrO$_2$ was used. $^{53}$Cr NMR measurements was performed by using a coherent pulsed spectrometer and a superconducting magnet. The frequency-swept NMR spectra were taken point by point in magnetic fields of $H_0 = 0$ and 0.4 T.

3. Results and discussion
Figure 2 shows $^{53}$Cr NMR spectra under zero external field at 4.2 K in the ferromagnetic insulating phase and at 110 K in the ferromagnetic metallic one of K$_2$Cr$_8$O$_{16}$. In a ferromagnetic state, NMR signals are generally observed from magnetic domains and/or domain walls with a large signal enhancement effect [7]. In K$_2$Cr$_8$O$_{16}$, the NMR spectrum observed at 4.2 K with the enhancement factor of ~200 is composed of four two-dimensional (2D) powder patterns Cr1-Cr4. Each pattern has double peaks as presented in Fig. 2 by the arrows which denote the Y and Z singularities of the internal field $H_n$, where the Y and Z axes are the principal axes of $H_n$, at the $^{53}$Cr nuclei located in the domain wall, if the domain wall is located in the YZ plane including the a and b axes. This spectrum assignment was clearly confirmed by the NMR spectrum, which shows a 3D powder pattern from the domain, in external fields (>0.5 T) where magnetization is saturated. Thus we can conclude that the zero-field NMR spectra at 4.2 K are the $^{53}$Cr domain-wall spectra from the four Cr sites which are consistent with the number of the crystallographically inequivalent Cr sites observed by the synchrotron x-ray measurement [8]. On the other hand, above $T_{MI}$, the four peaks from the domain wall were observed as seen
in Fig. 2. Although we could not make the site assignment for the NMR spectrum at 110 K, it clearly shows at least two Cr NMR spectra with internal fields different from each other. This finding is inconsistent with the tetragonal lattice symmetry $I4/m$ with the crystallographically inequivalent one Cr site, which is expected to result in one NMR spectrum, above $T_{MI}$.

![Figure 2](image)

**Figure 2.** (Color online) (a) Zero-field $^{53}$Cr NMR spectra at 4.2 and 110 K in $K_2Cr_8O_{16}$. The arrows indicate the positions of the $Y$ and $Z$ singularities in the 2D powder patterns of the Cr1-Cr4 spectra.

![Figure 3](image)

**Figure 3.** (Color online) $^{53}$Cr NMR spectra with $H_0 = 0$ and 0.4 T at 4.2 K in $CrO_2$.

In the ferromagnetic metallic phase of $CrO_2$, a similar NMR spectrum to that in $K_2Cr_8O_{16}$ was observed as seen in Fig. 3 which shows the $^{53}$Cr NMR spectra at 4.2 K for $H_0 = 0$ and 0.4 T. The zero-field spectrum has two sharp peaks located at 26.5 and 37.2 MHz as reported in Ref. 9. Although we cannot clarify whether the peaks come from $^{53}$Cr nuclei in the domain wall or not, the NMR spectrum at 0.4 T cannot be reproduced by only one 3D powder pattern.
with the $X$, $Y$ and $Z$ singularities coming from the domain. This means that there are at least two Cr sites with $H_n$ different from each other. This observation is inconsistent with one Cr site in the rutile structure (space group $P4_2/mnm$) of CrO$_2$. Thus the NMR spectra observed in K$_2$Cr$_8$O$_{16}$ and CrO$_2$ indicate the presence of the anomalous electronic state which may appear commonly in the double exchange systems within the negative charge transfer region.

Finally we discuss the origin of the anomalous electronic state observed in the half-metallic chromium oxides K$_2$Cr$_8$O$_{16}$ and CrO$_2$. One possible origin is the electronic phase separation which may be induced in the double exchange systems such as the Mn oxides, La$_{1-x}$A$_x$MnO$_3$ ($A =$ Sr and Ca), where the phase separation was discussed on the basis of the competition between the electron localization due to the antiferromagnetic correlation and the delocalization in the ferromagnetic region [3]. Also onsite and intersite coulomb interactions may contribute to the anomalous electronic state. The second one is the charge fluctuation at a frequency lower than the NMR frequency as Shim et al. argued for CrO$_2$ [9]. Theoretical studies are highly desired to understand the anomalous electronic state observed in the present NMR experiments on K$_2$Cr$_8$O$_{16}$ and CrO$_2$.

4. Conclusion

We performed $^{53}$Cr NMR measurements on the ferromagnetic half-metals K$_2$Cr$_8$O$_{16}$ and CrO$_2$ to clarify the local electronic states. In the ferromagnetic metallic phase of both chromates, we found that there are at least two Cr sites with the electronic states different from each other in spite of one Cr site in the tetragonal crystal symmetry. This may be a peculiar phenomenon of chromium oxides with the negative charge transfer in the double exchange systems.

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