Observation of lattice dimerization in spin-singlet low temperature phase of $NaTiSi_2O_6$

E.Ninomiya [a,1], M.Isobe [b], Y.Ueda [b], M.Nishi [c], K.Ohoyama [d], H.Sawa [e], T.Ohama [a]

[a] *Graduate School of Science and Technology, Chiba University, Chiba 263-8522, Japan*
[b] *Material Design and Characterization Laboratory, ISSP, University of Tokyo, Kashiwa 277-8581, Japan*
[c] *Neutron Scattering Laboratory, ISSP, University of Tokyo, Tokai 319-1106, Japan*
[d] *Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*
[e] *Photon Factory, Institute of Materials Structure Science, KEK, Tsukuba 305-0801, Japan*

Abstract

$NaTiSi_2O_6$ is a spin-1/2 member of the quasi-one-dimensional magnets; pyroxene family. This compound exhibits the phase transition at 210 K, which is accompanied by the structural change and the spin-singlet formation. The alternation of Ti-Ti distance within the chain made up of edge-shared TiO_6 octahedra in the low temperature phase was observed in x-ray and neutron diffraction. This is the direct evidence for the formation of Ti^{3+}-Ti^{3+} singlet pairs.

Key words: $NaTiSi_2O_6$; quasi 1-D magnet; spin-singlet ground state; structural transition

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The alkali metal pyroxene compounds denoted as $AM^{3+}B_2O_6$ ($A =$ alkali metal; $B =$ Si, Ge; $M =$ cations with valence state of 3+) are quasi-one-dimensional (1D) magnets. The structure includes isolated zigzag chains made up of edge-sharing MO_6 octahedra. Since the crystallographic M^{3+}-cation site is unique in the structure, the chains can be regarded as uniform linear chains. Each chain is bridged by SiO_4- or GeO_4-tetrahedra and alkali metal ions A^+ occupy the tunnel sites in the framework formed by MO_6-octahedra and BO_4-tetrahedra. Almost transition metal compounds of the pyroxene family exhibit Néel ordered states as the ground state.

$NaTiSi_2O_6$ is a spin-1/2 (Ti^{3+}) member of the alkali metal pyroxene family. It crystalizes in the space group $C2/c$ with a monoclinic symmetry at room temperature [1]. Recently a transition at $T_c \sim 210$K was observed in the title compound [2]. The transition is characterized by the decrease of magnetic susceptibility and thermal and structural change. The low temperature phase was identified to be triclinic. The ground state is a spin singlet. The transition is similar to the spin-Peierls transition in certain characteristics but is different in some properties. The most significant feature is that the transition occurs at a temperature higher than that at the maximum point of the Bonner-Fisher curve. This means that the short-range magnetic correlations within the chain are not fully developed and intrinsic magnetoelastic instability of a 1D system cannot be considered as a driving force for the transition. Furthermore the crystallographic evidence for the formation of Ti^{3+}-Ti^{3+} singlet pairs within the chain has not been obtained. We have studied the crystal structure of the low temperature phase by means of x-ray and neutron diffraction. In this paper we report clear evidence for the dimerization within the chain.

A polycrystalline sample was prepared by a conventional solid-state reaction [2]. We performed neutron powder diffraction experiments by using the Kinken powder diffractometer for high efficiency and high resolution measurements, HERMES, of Institute for Materials Research(IMR), Tohoku University, installed at

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[1] E-mail:nino@physics.s.chiba-u.ac.jp

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the JRR-3M reactor in Japan Atomic Energy Research Institute (JAERI), Tokai [3]. Neutrons with a wavelength of 1.8196 Å were obtained by the 331 reflection of the Ge monochromator. The fine powder sample was sealed in a vanadium cylinder with helium gas, and mounted at the cold head of a closed cycle He-gas refrigerator. The diffraction data were integrated for 6.5 hours at intervals of 0.05 °. We collected diffraction patterns in the range of 10K to 300K. Although it has not determine whether the structure has inversion symmetry, we analyzed diffraction patterns with a triclinic symmetry ($P\bar{1}$) using the RIETAN-2000 program [4]. We obtained a satisfactory agreement between the observed and calculated intensities (for example, R_{wp} = 7.80%, R_{I} =4.67% at 300K and R_{wp} = 9.80%, R_{I} =6.61% at 100K)

The obtained lattice parameters are a=9.6955(3)Å, b=8.8851(2)Å, c=5.2968(2)Å, β=106.720(2)° at 300K and a=6.627(1)Å, b=8.845(2)Å, c=5.2895(4)Å, α=90.180(1)°, β=102.230(1)°, γ=47.034(1)° at 100 K. Figure 1 shows the schematic drawing of the chain made up of edge-shared TiO_6 octahedra above (300 K) and below (100 K) the transition temperature.

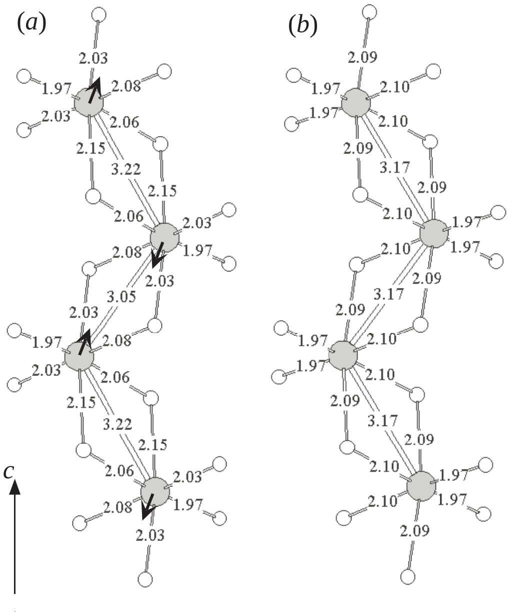

Fig. 1. Schematic representation of the structure for $NaTiSi_2O_6$ at (a)100K (b)300K. Full circles show Ti ions and open circles are O ions. Arrows indicate roughly the direction of displacements.

There exist two crystallographically independent sites for Ti atom in the structure of the low temperature phase. From the analysis of the diffraction data, we found the alternation of Ti-Ti distance within the chain in the low-temperature phase, as shown in Fig. 1(a). This indicates the formation of dimer, which is consistent with the spin singlet ground state. Figure 2 shows the Ti-Ti distance as a function of temperature. The alternation of the Ti-Ti distance clearly starts at $T_{\mathrm{c}} \sim$ 210K and gradually increase with decreasing temperature, indicating the gradual development of the formation of Ti^{3+}-Ti^{3+} singlet pairs.

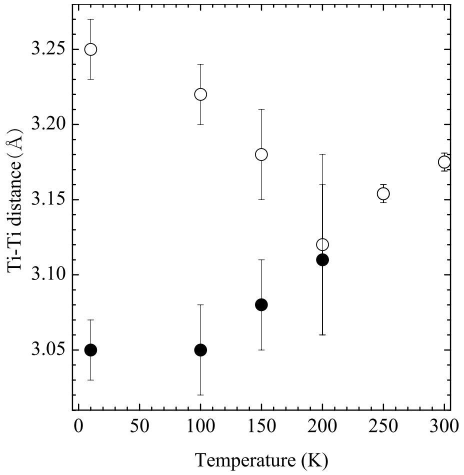

Fig. 2. The distances between Ti ions along chains in $NaTiSi_2O_6$ as a function of temperature.

In summary we studied the crystal structure of $NaTiSi_2O_6$ by means of x-ray and neutron diffraction in the temperature range 10K to 300K, and we found the alternation of Ti-Ti distance within the chain made up of edge-shared TiO_6 octahedra in the low temperature phase. This is the direct evidence for the formation of Ti^{3+}-Ti^{3+} singlet pairs.

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