Optical conductivity of Ca$_{1-x}$Na$_x$V$_2$O$_4$ ($x = 0$, 2/3 and 1)

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Abstract. Optical conductivity was measured for CaV$_2$O$_4$, Ca$_{1/3}$Na$_{2/3}$V$_2$O$_4$ and NaV$_2$O$_4$. The spectra of CaV$_2$O$_4$ showed insulating behavior with the band gap of 0.07 eV, which agrees well with the energy gap estimated from electrical resistivity data. On the other hand, in the spectra of NaV$_2$O$_4$, Drude peak was clearly observed at 300 K and 8 K, supporting the metallic nature below and above antiferromagnetic transition at 140 K. For Ca$_{1/3}$Na$_{2/3}$V$_2$O$_4$, the spectrum at 300 K showed Drude peak, while that at 8 K showed insulating behavior with the band gap of 0.08 eV. This change is caused by metal-insulator transition observed by the resistivity measurement.

1. Introduction
Both CaV$_2$O$_4$ and NaV$_2$O$_4$ crystallize in calcium ferrite type structure, which is shown in Fig. 1, but their physical properties are contrastive to each other. CaV$_2$O$_4$ is electrically insulating, and shows antiferromagnetic transition at $T_N = 78$ K [1]; the temperature apparently depends on the samples probably due to calcium deficiency [2]. Magnetic susceptibility shows a broad maximum at around 300 K because of one dimensional spin correlation and/or spin frustration in the double chains of V$_2$O$_4$. Magnetic structure was determined by detailed NMR and neutron diffraction measurements [1, 3]; magnetic moments are aligned almost perpendicular to the chain directions. On the other hand, NaV$_2$O$_4$ shows antiferromagnetic transition at $T_N = 140$ K maintaining metallic conductivity [4]. The antiferromagnetic phase is composed, at least, of three kinds of subphases, whose boundary is very sensitive to temperature and magnetic field [5]. According to $\mu$SR, Neutron diffraction, and NMR measurement, magnetic moments in the ground state are helically rotating with incommensurate propagation vector (0 0.191 0) [6, 7, 8]. The purpose of our study is to make clear the physical properties which appear in the solid solution system Ca$_{1-x}$Na$_x$V$_2$O$_4$.

This workshop was supported in part by the Grant-in-Aid for the Global COE Program “The Next Generation of Physics, Spun from Universality and Emergence” from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan.
2. Experimental

CaV$_2$O$_4$ was synthesized in flowing H$_2$ gas at 1000°C for 6 hours from CaV$_2$O$_6$, which was prepared from a stoichiometric mixture of CaCO$_3$ and V$_2$O$_5$ at 700°C in air. The powder sample obtained was pressed under high pressure of 6 GPa using a belt-type press and heated at 1300°C for 1 hour to obtain a hard pellet for optical conductivity measurement. On the other hand, Ca$_{1/3}$Na$_{2/3}$V$_2$O$_4$ and NaV$_2$O$_4$ were made by high pressure synthesis technique from stoichiometric mixtures of CaV$_2$O$_4$, Na$_4$V$_2$O$_7$ and V$_2$O$_3$. The mixtures were sealed in Au capsules in a dry box filled with Ar gas because Na$_4$V$_2$O$_7$ is reactive with moisture in air. Then,
Figure 3. Optical conductivity of CaV$_2$O$_4$ (a), Ca$_{1/3}$Na$_{2/3}$V$_2$O$_4$ (b), and NaV$_2$O$_4$ (c) as a function of photon energy. In each panel, the black and red lines represent the data at 8 K and 300 K, respectively. The blue dotted lines in panel a and b are guides to eye to show the position of the edges of the interband excitation.

the samples were pressed under 6 GPa and heated at 1300°C for 1 hour. After the synthesis, they were quenched to room temperature and then the pressure was gradually released to ambient pressure. Na$_4$V$_2$O$_7$ was prepared from a stoichiometric mixture of NaCO$_3$ and V$_2$O$_5$ by heating it at 550°C in air with intermediate grindings. V$_2$O$_3$ was obtained by reduction of V$_2$O$_5$ by flowing H$_2$ gas.

Magnetic susceptibility data were collected under magnetic field of 1 T using a commercial magnetometer, MPMS-XL (Quantum Design). Electrical resistivity was measured by conventional four probe method in PPMS (Quantum Design). Optical conductivity was obtained from reflectivity of wide energy range by Kramers-Kronig analysis. The reflectivity was measured at 8 K and 300 K using an FT-IR spectrometer with conventional light sources for the photon energy up to 1.5 eV.

3. Results and Discussion

Figure 2 shows magnetic susceptibility and electrical resistivity of Ca$_{1-x}$Na$_x$V$_2$O$_4$. The peak of the susceptibility of NaV$_2$O$_4$ corresponds to the antiferromagnetic transition [6, 7, 9], and the peak temperature decreases with decreasing $x$ down to $x = 0.78$. At this $x$ range, electrical resistivity shows no significant change as a function of chemical composition or temperature. Thus, the metallic antiferromagnetic state is preserved for $x > 0.78$, which is supported by other experiments [6, 7, 8, 9]. On the other hand, as the $x$ value further decreases down to about 0.3, the peak temperature of magnetic susceptibility, $T_{\text{max}}$, rapidly increases and reaches around 300 K. In addition, electrical resistivity markedly increases below $T_{\text{max}}$, suggesting metal-insulator transition. Thus, electronic ground state for $\sim 0.3 < x < 0.78$ is completely different from
that for \( x > 0.78 \). Below \( x \sim 0.3 \), \( T_{\text{max}} \) slightly decreases as seen in Fig. 2c, but no clear metal-insulator transition was observed below 400 K any longer. The band gap for \( x < 0.78 \) was roughly estimated to be \( \Delta \sim 1000 \) K from the slope of Arrhenius plot.

Because electronic state of \( \text{Ca}_{1-x}\text{Na}_x\text{V}_2\text{O}_4 \) is separated into three kinds depending on the \( x \) value, optical conductivity was measured for the \( x = 0, 2/3 \) and 1 samples at 8 K and 300 K. The spectra obtained are shown in Fig. 3. In all of them, the sharp peaks were observed around \( E = 0.05 \) eV, which originate from phonons. For \( \text{NaV}_2\text{O}_4 \) (\( x = 1 \)), finite spectral weight is seen at \( E = 0 \) eV at both 8 K and 300 K, which is due to Drude contribution and is consistent with the metallic behavior below and above \( T_N \). On the other hand, the spectra at 8 K and 300 K for \( \text{CaV}_2\text{O}_4 \) (\( x = 0 \)) have no Drude term, indicating insulating nature of it. The conductivity starts increasing at \( E = 0.07 \) eV, which agrees well with \( \Delta \) (0.086 eV). Thus, the increase is due to interband excitation. For \( \text{Ca}_{1/3}\text{Na}_{2/3}\text{V}_2\text{O}_4 \) (\( x = 2/3 \)), the spectrum at 300 K is similar to that of \( \text{NaV}_2\text{O}_4 \), showing metallic nature, while that at 8 K clearly indicates that the band gap opens as in the case of \( \text{CaV}_2\text{O}_4 \). The spectral change is due to metal-insulator transition seen in the resistivity. The band gap was estimated to be 0.08 eV, from the edge of the broad peak around \( E = 0.7 \) eV.

4. Conclusion
Magnetic susceptibility and electrical resistivity were measured for \( \text{Ca}_{1-x}\text{Na}_x\text{V}_2\text{O}_4 \), and it was proved that electronic state is separated into three kinds depending the \( x \) value. For \( x > 0.78 \), the metallic antiferromagnetic ordered state occurs, for \( x < \sim 0.3 \) the insulating behavior was observed at the entire temperature region below 400 K, and for \( \sim 0.3 < x < 0.78 \), the metal-insulator transition appears. These were confirmed by the optical conductivity measurement. The band gap of the insulating state for \( x = 0 \) and 2/3 was estimated to be 0.07 eV and 0.08 eV, respectively, which agree well with the slopes of Arrhenius plot of the resistivity.

Acknowledgments
Special thanks to Dr. Taniguchi (NIMS) for his support for high pressure synthesis. This work was supported in part by Grant-in-Aid for Scientific Research (A) from Japan Society for the Promotion of Science (JSPS) (22246083), by Grant-in-Aid for Scientific Research from MEXT (19560665), and by FIRST from JSPS. The authors thank the Yukawa Institute for Theoretical Physics at Kyoto University, where this work was completed during the YITP-W-10-12 on "International and Interdisciplinary Workshop on Novel Phenomena in Integrated Complex Sciences: from Non-living to Living Systems".

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