Charge Ordering in Vanadium Compound

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1. Introduction

Vanadium compound shows a variety of characteristics concerning the charge valence state. V_2O_5 and CaV_2O_5 are typical examples. V in V_2O_5 is believed to be +5, while that in CaV_2O_5 is +4. Our interest is that how are the valence numbers of V atoms in LiV_2O_5, NaV_2O_5, CsV_2O_5 and $Sr_{1/2}V_2O_5$ in general. Special attention was paid to the structural view point as well as the spin-Peierls phase transition of NaV_2O_5. The structure of these compounds are already reported, but there was no clear experimental evidence to reveal the valence state of vanadium atom. Not only that, recent structure analysis on NaV_2O_5 gave an objection to the reported structure.

2. Experimental

XAFS measurements were carried out at the Crystal Structure Analysis beam-line (BL02B1) in the SPring-8 to pin down the energy of the absorption edge of Vanadium atom. In addition, X-ray diffraction studies were performed at the same beam line. We used the double-Si111 monochromator and the double-mirror to reduce the higher order contamination. Vacuum path was put in from the front-end to sample position. For XAFS measurements, powder samples were used. They were attached in two mending-tapes and settled between two ionization chambers. Single crystals of LiV_2O_5 and NaV_2O_5 were put in a vacuum chamber camera. Oscillation photographs were taken with 25keV X-ray and around 5keV ones. Ring current was about 16mA. All measurements were performed at the room temperature. Samples are prepared by Dr. Isobe and Dr. Ueda of ISSP the University of Tokyo.

3. Results and Discussion

The structure analysis of LiV_2O_5 and NaV_2O_5 is still under waiting since the program DENZO which is dedicated to the Image-plate of this vacuum camera was not installed yet at BL02B1.

We have taken XAFS patterns around the vanadium atom. Enlarged figures around the pre-edge are summarized in Fig.1. As shown in Fig.1, the energy position of the pre-edge clearly shows some characteristics depending on the valence state of Vanadium atom. The energy difference between +4(CaV_2O_5) and +5(V_2O_5) is 1.7eV and the energy difference between metallic one and +4(CaV_2O_5) is 2.3eV.

We analyzed that LiV_2O_5 and/or NaV_2O_5 has two components of the pre-edge corresponding to the mixed valence sate. For LiV_2O_5, we could successfully fit the curve with two peaks, and one-peak model looks worse than that of two-peak model. On the other hand, for NaV_2O_5, it is hard to distinguish two alternative models. Both model looks good enough so that we can not identify the valence state in NaV_2O_5. One of the reason is that the energy resolution is slightly poor to archive the final result, and also we could not change the temperature since the cryostat at BL02B1 has a Beryllium window. Further experiments are definitely required to get the clear results.

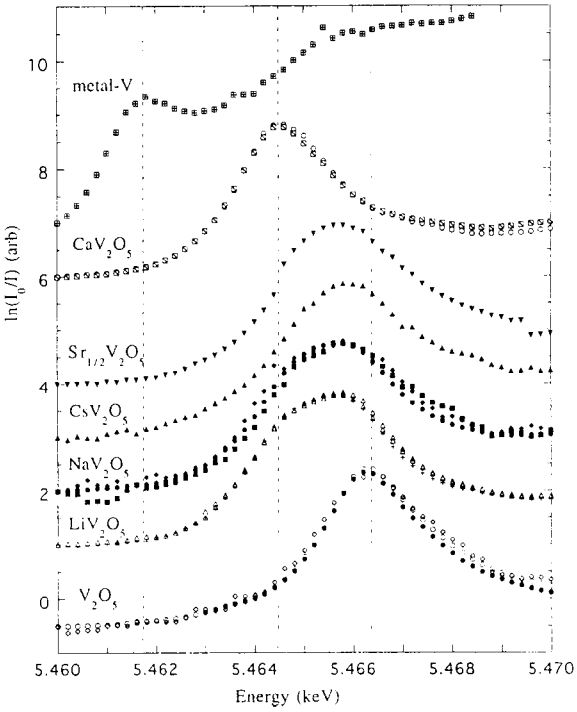

Fig.1 Pre-edge of Vanadium compounds