Pressure-Induced Phase Transition of $Na_{0.99}V_2O_5$ at Low Temperature

Yuya KATSUKI, Yasuhiko FUJII*, Naohisa TAKESUE, Masahiko ISOBE, Yutaka UEDA, Kenji OHWADA[1], Hironori NAKAO[2], Yusuke WAKABAYASHI[3], Youichi MURAKAMI[4], Kazuki ITOH[5], Yoshiyuki AMEMIYA[6], Hiroshi FUJIHISA[7], Katsutoshi AOKI[7]
Institute for Solid State Physics, The University of Tokyo, Kashiwa, Chiba 277-8581, Japan
[1]Kansai Research Establishment, JAERI, Sayo, Hyogo 679-5148, Japan
[2]KEK-PF, Tsukuba, Ibaraki 305-0801, Japan,
[3]Faculty of Science, Chiba University, Chiba, Chiba 263-8522, Japan
[4]Graduate School of Science, Tohoku University, Sendai 980-8578, Japan
[5]Institute of Applied Biochemistry,The University of Tukuba, Tukuba, Ibaraki 305-3587, Japan
[6]Department of Applied Physics, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan
[7]National Institute of Materials and Chemical Research, Tukuba, Ibaraki 305-8565, Japan

Since 1996 the inorganic compound NaV_2O_5 has drawn much attention because of it's spin-Peierls-like behavior[1]. It has an orthorhombic structure with lattice constants a=11.325Å, b=3.611Å,c=4.806Å. In the ab-plane VO_5-pyramids form two-dimensional networks sharing its corners or edges. Such network layers are stacked along the c direction with Na atoms intercalated.

Recently it is well understood that NaV_2O_5 undergoes an order-disorder phase transition associated with charge on V ions cooperatively coupled with spin-gap formation, and lattice dimerization ($2a\times2b\times4c$) at T_c=35K under ambient pressure[2, 3].

Very recently Ohwada et al.[4] carried out x-ray scattering experiments and reported that at high pressures and low temperatures NaV_2O_5 shows a large variety of phases, all of which have $2a\times2b\times zc$ type modulated structure. Thus obtained P-T phase diagram resembles the "devil's staircase" or "devil's flower" theoretically obtained ANNNI model.

In this paper to investigate the charge imbalance effect on V we report the detailed SR x-ray study of $Na_{0.99}V_2O_5$ at high pressures ($P < 1.5GPa$) and low temperatures ($T < 30K$), which is deficient in an electron donor Na by 1%.

The x-ray scattering experiments were carried out both at BL-1B (Micro Powder Diffractometer) and BL-4C (four-circle diffractometer). Wavelength was tuned to 0.69Å with a Si(111) monochromator. A diamond anvil cell (DAC) which was mounted on a closed-cycle helium refrigerator with a 4:1 mixture of methanol/ethanol as pressure media was used. Pressure and temperature were monitored from the lattice constant of NaCl and with a Au-0.07%Fe chromel thermocouple, respectively. We used high-quality $Na_{0.99}V_2O_5$ single crystals which were grown by a flux method with a typical size of 100μm ×500μm ×50μm.

We found a systematic appearance of the $2a\times2b\times zc$ (z=1,4,5,$\frac{21}{4}$,6,8) type phases similar to the case of pure system NaV_2O_5. Figure 1 shows the pressure-temperature phase diagram of $Na_{0.99}V_2O_5$. In Fig. 1 the open circles indicate the points where phase tranditins were monitored. The areas named P and $C_{\frac{1}{z}}$ show normal phase which is observed up to room temperature at ambient pressure and commensurate phases with the modulation wave vector q=($\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{z}$), respectively. The shaded area shows more complicated higher-order commensurate or incomensurate phase. The broken lines indicate the outline of phase diagram of pure system.

The P-T phase diagram of $Na_{0.99}V_2O_5$ can be reproduced by shifting that of NaV_2O_5 by -5K along T and -0.1GPa along P. Such a remarkable effect may give a clue for a microscopic mechanism of competitive interactions in this system leadeing to the "devil's staircase" type behavior.

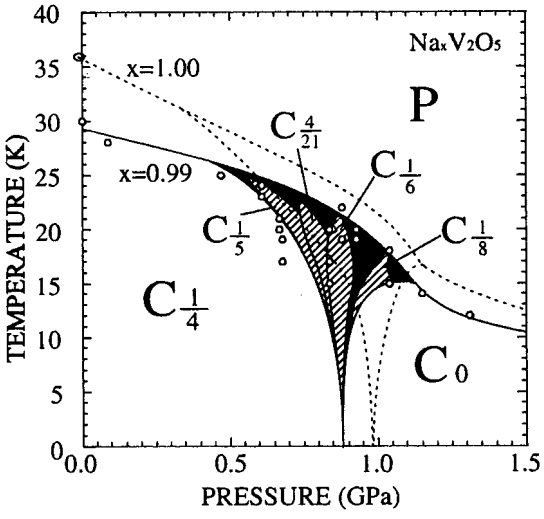

Fig. 1: P-T phase diagram of $Na_{0.99}V_2O_5$

References

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*yfujii@issp.u-tokyo.ac.jp