X–ray study of modulated structures of β'–$Cu_xV_2O_5$ ($x = 0.29, 0.39$)

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Abstract

High resolution X-ray study reveals the wave vector change in the modulated structure of the quasi-one dimensional compound β'–Cu vanadium bronze. Structural modulation of the reduced wave vector $\boldsymbol{q}_0 = (0, 0.305, 0)$ emerges below 220 K in β'–$Cu_{0.29}V_2O_5$. For β'–$Cu_{0.39}V_2O_5$, not the single $\boldsymbol{q}$ modulation but two kinds of modulations were observed. A three–fold superlattice structure with $\boldsymbol{q}_1 = (0, 0.333, 0)$ appears below 210 K. An incommensurate modulated structure with $\boldsymbol{q}_2 = (0, 0.26 \sim 0.29, 0)$ coexists below 175 K, whose satellite intensity and b^*component Q_b have temperature and passing-time dependencies between 140 K and 175 K. The competition between $\boldsymbol{q}_1$ and $\boldsymbol{q}_2$ modulations was also observed. It seems that the $\boldsymbol{q}_2$ is deeply related to the physical property change between 140 K and 180 K confirmed by the decrease in the magnetic susceptibility and the increase in the resistivity.

Key words: X-ray, modulated structure, low dimensional conductor, vanadium bronze, β'–$Cu_xV_2O_5$,

1. Introduction

β and β' type vanadium bronzes have a quasi-one dimensional crystal structure with the space group *C2/m*. There are three sites for vanadium(V1,V2,V3); V1 forms a zig-zag chain by sharing the edges of VO_6 octahedron. V2 forms a two leg ladder by sharing the corners of VO_6 octahedron. V3 forms another zig-zag chain sharing the corners of VO_5 pyramid. These chains and ladder run along the *one-dimensional* $\boldsymbol{b}$–axis. Metal ion is inserted in the tunnel formed by V_2O_5 framework[1]. β type vanadium bronze has been investigated systematically and its electronic property has been understood in terms of a bipolaron formation in the V1 chain[2]. Knowledge of physical properties of β' type bronze was limited, modulated structures observed in β'–$Cu_xV_2O_5$ have been also explained in terms of the bipolaron ordering[3]. However, recent magnetic measurement of vanadium bronze showed not the bipolaron spin-singlet state but another *magnetic* ground state[4]. Furthermore Yamada *et. al* presented electrical, magnetic and structural properties of β'–$Cu_xV_2O_5$ systematically[5]. β'–$Cu_xV_2O_5$ is a quasi one-dimensional conductor for $x > 0.60$ but a semiconductor for low Cu concentration. Around $x = 0.40$, anomaly in the activation energy has been observed. Modulated structure formation and anomalies in the resistivity and the magnetic susceptibility have been observed around 210 K for $x = 0.29$. For $x = 0.39$, both an increase in the resistivity and a decrease in the magnetic susceptibility which depend on the cooling rate, have been observed between 140 K and 180 K. Furthermore a change in the periodicity of the modulated structure has been observed. To understand these relationship between physical properties and structure, we performed high resolution X-ray measurement of $x = 0.29$ and $x = 0.39$ using HUBER 5042 four-circle diffractometer and single crystals grown by the improved method.

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2. Results and Discussion

Figure 1 shows temperature dependencies of the integrated intensities of the first-, second- and third-order satellite reflections observed in β'–$Cu_{0.29}V_2O_5$.

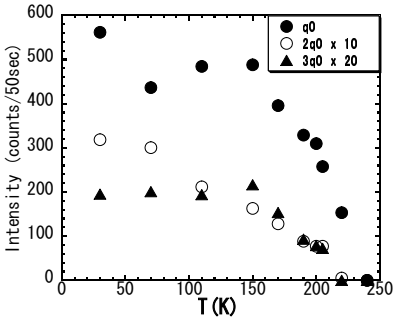

Fig. 1. Temperature dependencies of the integrated intensities of the first-, second- and third-order satellite reflections of β'–$Cu_{0.29}V_2O_5$.

These reflections are located at $\boldsymbol{Q}_{\pm n} = \boldsymbol{G} \pm n\boldsymbol{q}_0$, where $\boldsymbol{G}$ is a reciprocal vector of the lattice and $\boldsymbol{q}_0 = (0, 0.305, 0)$. Within the experimental accuracy, we observed no temperature dependence of $\boldsymbol{q}_0$. Difference in the width between of satellite reflections and of fundamental ones indicates that the structural correlation length is more than 1000 $\AA$. Since intensities of the second- and third-order satellite reflections are relatively strong, these reflections are not due to the diffraction harmonics(Bessel function contribution) but the inharmonicity of the modulation. In other words, the modulation is not sinusoidal.

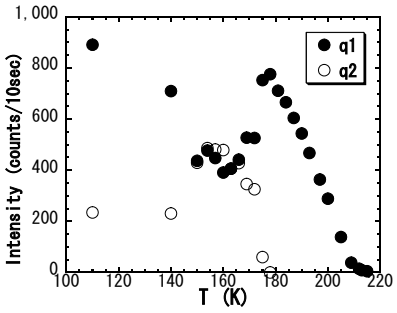

Fig. 2. Temperature dependencies of the integrated intensities of satellite reflections of β'–$Cu_{0.39}V_2O_5$. The successive measurements were performed on heating process after slow cooling of 0.5 K/min. The temperature of the crystal was hold during five hours for one measurement, and heating rate between measurements was 0.1 K/min.

Figure 2 shows temperature dependencies of the integrated intensities of two kinds of satellite reflections observed in β'–$Cu_{0.39}V_2O_5$. Satellite reflection with the commensurate wave vector of $\boldsymbol{q}_1 = (0, 0.333, 0)$ is present below 210 K. Satellite reflection with the incommensurate $\boldsymbol{q}_2 = (0, 0.26 \sim 0.29, 0)$ coexists below 175 K. Both the satellite intensity and the b^* component Q_b of $\boldsymbol{q}_2$ have temperature and passing-time dependencies between 140 K and 175 K. Both of them increase with the passage of time at 160 K. Below 175 K the $\boldsymbol{q}_1$ satellite intensity decreases with the evolution of the $\boldsymbol{q}_2$ modulation. On the other hand, below 140 K the $\boldsymbol{q}_1$ modulation become dominant with the decrement of the $\boldsymbol{q}_2$ modulation. This indicates these modulations are not independent.

Then we will survey the structural modulations ever observed in β'–$Cu_xV_2O_5$ of the lower doping level x. For $x = 0.29$, the inharmonic modulation of $\boldsymbol{q}_0 = (0, 0.305, 0)$ is observed. Similarly For $x = 0.32$, the inharmonic modulation of $\boldsymbol{q} = (0, 0.325, 0)$ has been observed[3]. This similarity suggests that these modulations have the common origin. With the increase of Cu doping level x, the Q_b increases, and the three-fold commensurate superstructure with $\boldsymbol{q}_1 = (0, 0.333, 0)$ appears for $x = 0.39$(this work) and $x = 0.40$[3]. Note that positive relation between the Q_b and the doping level x. This modulation may be originated from the Cu configurational ordering. This ordering of the metal has been proposed for the superstructures observed in several β and β' type vanadium bronzes[5]. Indeed, this proposal is plausible for several vanadium bronzes. However, this seems not the case in this β'–Cu vanadium bronze. This is because the Q_b is not equal to $1.5x$. From the chemical formula and the crystal structure, the wave vector of metal site ordering should be equal to 1.5 times x. In all the β'–Cu vanadium bronze above, the Q_b is too small compared with $1.5x$. In fact, there is no apparent indication of the Cu ordering in the three-fold superstructure for $x = 0.39$[6]. Alternatively, from the gradual increase in Q_b with the value of the doping level, this modulated structure may be related to carrier number in the V_2O_5 framework.

Finally, the incommensurate modulated structure $\boldsymbol{q}_2$ with smaller Q_b of $0.26 \sim 0.29$ is very particular and observed only in the $x = 0.39$ vanadium bronze. Although the origin of the modulation remains unclear, this modulated structure will be related to the decrement in the magnetic susceptibility and the increment in the resistivity[5] observed in the same temperature range of the $\boldsymbol{q}_2$ modulation prominence.

References

[1] A. -M. Savariault *et. al*, Z. fur Kristal. **209** (1994) 405.

[2] H. Nagasawa *et. al*, J. Phys. Coll. C3. **44** (1983) 1737.

[3] Y. Kanai *et. al*, Synth. Met. **9** (1984) 369.

[4] H. Yamada *et. al*, J. Phys. Soc. Jpn. **68** (1999) 2735.

[5] H. Yamada *et. al*, J. Phys. Soc. Jpn. **69** (2000) 1437.

[6] N. Nagao *et. al*, in preparation.