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PHASE TRANSITION IN $V_{1+x}Te_2$ ($0.04 \leqslant x \leqslant 0.11$)

T. Ohtani, K. Hayashi and M. Nakahira

Okayama College of Science, Laboratory for Solid State Chemistry, 1-1 Ridaicho. Okayama 700, Japan

and

H. Nozaki

National Institute for Researches in Inorganic Materials, 1-1 Namiki, Sakuramura, Niihari-Gun, Ibaraki, Japan

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1T–$V_{1+x}Te_2$ was synthesized in a composition range of $0.04 \leqslant x \leqslant 0.11$. The reversible first order transition was observed by DTA (DSC), powder X-ray diffraction, magnetic susceptibility (χ), and d.c. electrical resistivity (ρ) measurements. Transition temperature (T_t) is 474 K for $V_{1.04}Te_2$, and decreases with increasing x. Heat of transition, ΔH was estimated to be as high as 500 cal mol^{-1} from the endothermical peak in DSC. The expansion of the c-axis is observed at T_t. χ exhibits a jump at T_t, showing the paramagnetic temperature dependence both below and above T_t. ρ measurements show the metallic-like behavior with a slight decrease at T_t. Preliminary electron diffraction examination suggests the formation of a super-structure below T_t.

1. INTRODUCTION

THE LAYERED TRANSITION-METAL dichalcogenides have been an interesting class of materials since they exhibit a rich variety of phase transitions [1]. One of the most interesting properties is the charge density waves (CDW) which was found in the Vth group transition-metal dichalcogenides [2]. Vanadium dichalcogenides, however, have received less attention except for 1T–VSe_2 which exhibits a CDW at 110 K [3, 4].

The most latest investigations on vanadium ditelluride were performed by Grönvold *et al.* and Röst *et al.* in 1958 [5] and 1964 [6], respectively, but no extensive investigation of this compound has hitherto been reported probably because of the difficulty of preparation. Grönvold *et al.* reported that the ditelluride phase, $V_{1+x}Te_2$, has an orthorhombic CdI_2-like structure with homogeneity range between $x = 0.08$ and 0.11. Within the composition range of $x < 0.08$, the orthorhombic phase coexisted with free tellurium. Röst *et al.* reported that the ditelluride phase exhibited the antiferromagnetic properties with the Néel temperature varying from 410 to 480 K.

The purpose of the present work is to establish the homogeneity range of the ditelluride phase and to reveal the nature of phase transition at about 410–480 K through the measurements of X-ray diffraction, DTA (DSC), magnetic susceptibility and electrical resistivity.

2. EXPERIMENTS

Powder specimens were prepared by heating appropriate mixtures of the elements in evacuated silica tubes at temperature 1073 K for 2 weeks, with the subsequent repetition of grinding and re-heating. The final products were obtained by slow cooling to room temperature at a rate of 5 K hr^{-1}. DTA and DSC data were obtained by an ordinary commercial apparatus, using samples in vacuum-sealed silica capsules. Magnetic susceptibility was measured by a Faraday type balance from 4.2 to 750 K. Electrical resistivity (d.c.) measurements were carried out on the pressed powders by an ordinary four-point probe method from 78 to 500 K.

3. RESULTS AND DISCUSSION

X-ray diffraction patterns of slowly cooled $V_{1+x}Te_2$ can well be indexed in terms of an orthorhombic cell except for very weak reflections, which is in accordance with that of Grönvold *et al.* [5]. Homogeneity range lies between $x = 0.04$ and 0.11. Its range spreads towards the tellurium richer composition than that reported by Grönvold *et al.* The lattice constants are; $a = 6.35$ A, $b = 10.78$ A, $c = 12.94$ A for $x = 0.04$, where $b \simeq 3a_{hex}$. A phase transition was observed in the thermal measurements (DTA and DSC) in the composition range, $0.04 \leqslant x \leqslant 0.09$. A typical DSC peak for $V_{1.05}Te_2$ is shown in Fig. 1. Heating and cooling rates are 10 K min^{-1}. Figure 2 shows the composition dependence

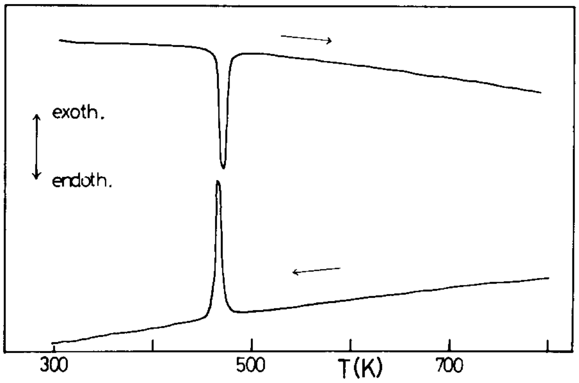

Fig. 1. DTA plot with slowly cooled $V_{1.05}Te_2$. Heating and cooling rates are $10\,K\,min^{-1}$. Al_2O_3 was used as a reference.

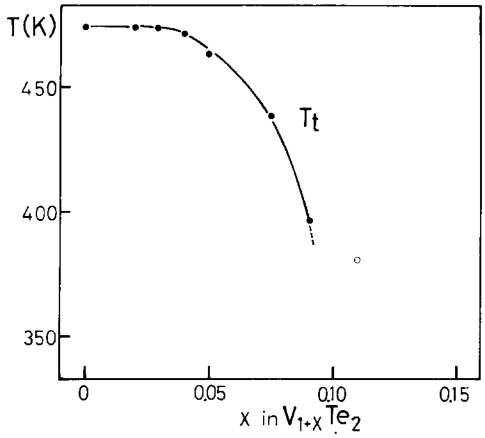

Fig. 2. Composition dependence of transiton temperature (T_t). Closed circles show the results obtained by DTA measurements. Open circle depicts the result from magnetic susceptibility measurements.

of the transition temperature (T_t) as observed in the heating runs. T_t is nearly constant through the region of $0 \leqslant x \leqslant 0.04$, which indicates the two-phase mixture of orthorhombic phase and free tellurium as observed in the X-ray diffraction. T_t continuously decreases with increasing vanadium content in the composition range of $x > 0.04$. DTA peak is very broadened for $x = 0.09$ and vanishes for $x = 0.11$. Enthalpy and entropy changes at T_t were obtained by DSC measurements. The apparatus was calibrated by using the known heats of fusion of Sn and In metals. The enthalpy and entropy change at the transition of $V_{1.045}Te_2$ are $505.0\,cal\,mole^{-1}$, $1.08\,cal\,deg^{-1}\,mole^{-1}$, respectively. ($V_{1.075}Te_2$: $\Delta H = 499.2\,cal\,mole^{-1}$, $\Delta S = 1.14\,cal\,deg^{-1}\,mole^{-1}$, $V_{1.09}Te_2$: $\Delta H = 78.1\,cal\,mole^{-1}$, $\Delta S = 0.20\,cal\,deg^{-1}\,mole^{-1}$).

The temperature dependence of the lattice constants was measured by the powder X-ray diffraction method. The expansion of the c-axis was observed at T_t

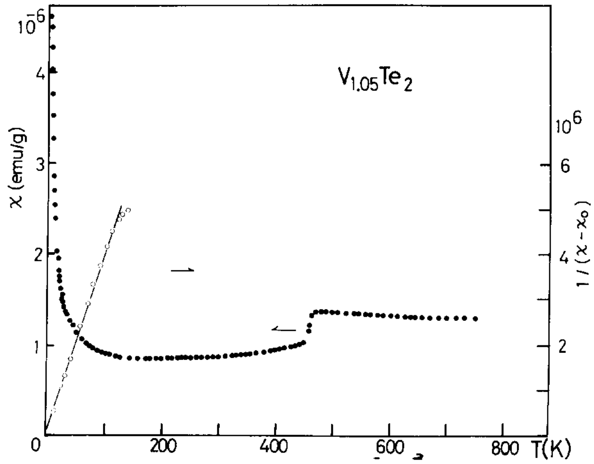

Fig. 3. Temperature dependence of magnetic susceptibility (χ) for $V_{1.05}Te_2$ from 4.2 to 750 K. Values of $1/(\chi - \chi_0)$ are also plotted, where χ_0 is the temperature-independent term.

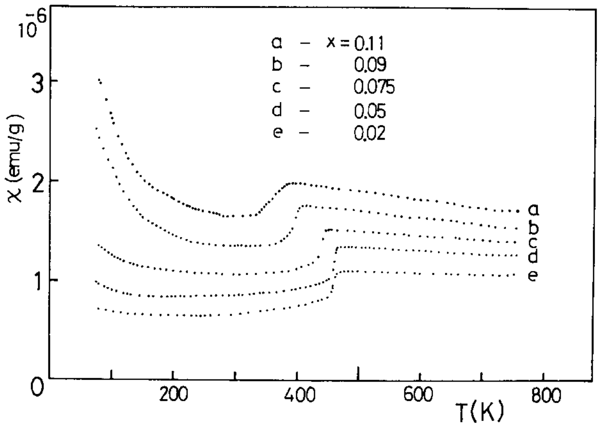

Fig. 4. Temperature dependence of magnetic susceptibility (χ) from 78 to 750 K for various compositions. The same anomaly for $x = 0.02$ and 0.05 is due to the two-phase region.

(about 1.0%). However, the detail of the diffraction pattern above T_t is still unknown due to the overlap of two different patterns, both based on the CdI_2-type structure. Figure 3 shows the temperature dependence of the magnetic susceptibility (χ) from 4.2 to 750 K for $V_{1.05}Te_2$. A jump of χ is observed at T_t. Below T_t, magnetic parameters were estimated by the equation, $\chi = \chi_0 + C/(T - \theta)$, where χ_0 is the temperature = independent term, C is the Curie constant and θ is the Weiss temperature. Data are well fitted on a straight line from 4.2 to about 100 K. We obtained the following parameters: $P_{eff} = 0.99\,\mu_B$, $\theta = -1.7\,K$ and $\chi_0 = 0.66 \times 10^{-6}\,emu\,g^{-1}$. Also above T_t, the data appears to obey the Curie–Weiss law, but we can not obtain reliable values of magnetic parameters because the data are relatively few. Figure 4 shows the temperature

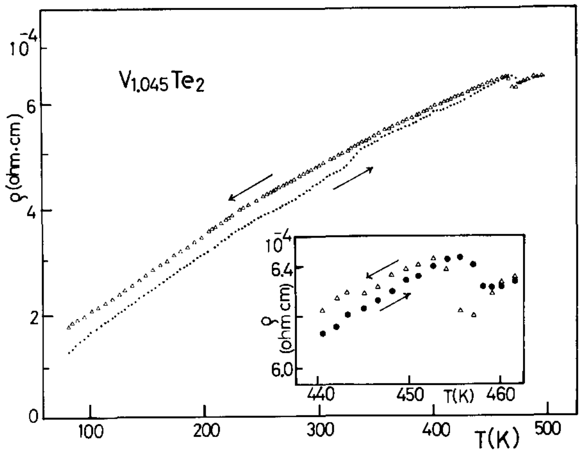

Fig. 5. Temperature dependence of d.c. electrical conductivity (ρ) from 78 to 500 K for $V_{1.045}Te_2$. The inset shows the detail near the transition. Heating and cooling rates are $1\,K\,min^{-1}$.

dependence of χ from 78 to 750 K for $0.02 \leqslant x \leqslant 0.11$. Anomaly was observed in all compositions corresponding to T_t observed in the above experiments. Below about 250 K, experimental values of χ are well fitted to the above equation. It is also notable that $V_{1.11}Te_2$ shows the anomaly which is undetectable in thermal measurements. These results are in contrast with the conclusion of Röst *et al.* who reported that the material was an antiferromagnet below T_t.

Figure 5 depicts the temperature dependence of d.c. electrical resistivity (ρ) for $V_{1.045}Te_2$. Measurements were carried out on pressed samples from 78 to 500 K with heating and cooling rates of $1\,K\,min^{-1}$. Results show metallic-like behavior in the whole temperature region, with slight decrease in ρ at T_t. Detail of ρ near T_t is shown in the inset. Transition has a hysteresis width of about 6 K. It is also remarkable that we can observe that another small anomaly in ρ in heating run at both about 230 and 330 K. Similar features were also observed in the other samples.

We summarize the characteristics of the transition of the representative $1T{-}V_{1+x}Te_2$, $x = 0.05$, at about 475 K. (1) The transition is of first order, and quite reversible. (2) The enthalpy change is about $500\,cal\,mole^{-1}$. (3) The expansion of the *c*-axis is observed at T_t. (4) Both below and above T_t, temperature dependence of χ exhibits the paramagnetic behavior, with an increase at T_t. (5) Temperature dependence of ρ shows the metallic-like behavior with a small decrease at T_t.

Layered compounds have generally a large variety of polytypes. $V_{1+x}Te_2$ has basically the CdI_2-type structure, which enables us to discuss this compound in comparison with the other 1T–type compounds. In the present case, the transition appears to be intra-polytipic one, since the value of heat of transition is relatively smaller than that of inter-polytipic transition [7]. Metallic-like behaviors both above and below T_t suggest that the transition is not due to the electron correlation effects but an induced small gap at the Fermi surface. We are strongly inclined to think that this is induced by CDW instability. In fact, our preliminary X-ray and electron diffraction studies indicate the formation of some superlattice within the low-temperature phase region.

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