Effects of Tungsten doping on the CDW states of η–Mo_4O_{11}

Takashi Kambe [a,1], Shizuko Tsuboi [a], Nobuaki Nagao [a], Yoshio Nogami [a], Kokichi Oshima [a]
[a] *GNST, Okayama University, 3–1–1 Tsushima, Okayama 700–8530, Japan*

Abstract

The η–Mo_4O_{11} system shows successive CDW transitions due to its two–dimensional Fermi surface instability. We find that the lower temperature CDW–II transition easily disappears by doping a small amount of W atoms (less than 0.2%/Mo), though the higher temperature CDW–I transition is weakly depressed. The W atoms possibly substitute both the intra– and the inter–layer Mo sites. The doping effectively reduce the carrier compensation, leading to the suppression of $T_{\mathrm{CDW-I}}$. Moreover, the interlayer coherence between the intralayer two–dimensional CDWs may be destroyed by the substitution between the layers since the modulation of CDW–II state has an interlayer component. The resistivity along the conducting plane follows "*log T*" dependence below 10 K, suggesting that the W atoms doped within the layer should induce the Anderson–type charge localization.

Key words: η–$(Mo_{1-x}, W_x)_4O_{11}$, CDW, Anderson localization,

1. Introduction

CDW transitions in η–Mo_4O_{11} successively occur at $T_{\mathrm{CDW-I}} = 109$K and $T_{\mathrm{CDW-II}} = 30$K. The conducting layer consists of MoO_6 octahedra, which elongate along three crystallographic directions b and $b \pm c$, and are separated by MoO_4 tetrahedra. The Fermi surface is considered to be the superposition of three "*hidden*" quasi–one–dimensional Fermi surfaces (FSs) [1]. The satellite reflections belonging to each CDW modulations had been measured by the X–ray scattering, and could be explained with the nesting vectors of this FS, as far as the components within the b^*c^*–plane [2]. However, the interlayer component of the CDW–II modulation cannot be reproduced and, then, the whole understanding of the ground state of these CDW states is not well done.

We tried to substitute Mo atoms by another atoms in order to control the position of FS. There is a little study on the impurity doping effects on the CDW states in η–Mo_4O_{11}, especially in the lower concentration region. We have succeeded in doping the isoelectric Tungsten (W) atoms with keeping the η–type crystal structure. In this paper, the effects of W doping on the each CDW states will be discussed.

2. Results and Discussion

The single crystals were synthesized by a vapor transport method. The stoichiometric mixed powders, which include both $TeCl_4$ and $MoCl_4$ as transporting agents, were sealed and put in a two–zone furnace, which temperatures were kept at 510°C and 470°C. Several single crystals grew around the low–temperature part of the furnace in a few weeks. In order to see a phase stability against doping W atoms, we also synthesized sintered samples as a function of W concentration. Then, we could not get a single phase of η–$(Mo_{1-x}, W_x)_4O_{11}$ system above $x = 0.01$. The transport measurements were done by a usual four–probe method. The resistivity within the conducting plane is remarkably sensitive to the contact configuration between these probes. This is possibly due to

[1] Corresponding author: Graduate School of Natural Science and Technology, Okayama University, 3–1–1 Tsushima, Okayama 700-8530, Japan. E-mail: kambe@science.okayama-u.ac.jp, fax: +81–86–251–7830

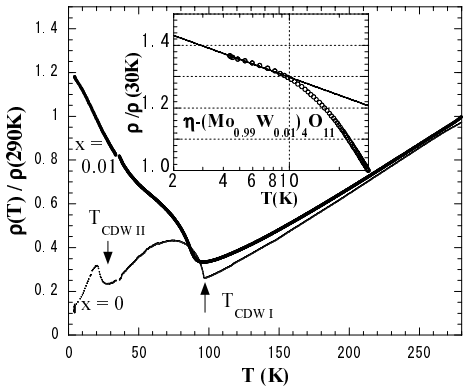

Fig. 1. In–plane resistivity of the single crystal η–$(Mo_{1-x}, W_x)_4O_{11}$ with $x = 0$ and 0.01. The electrical current is along the b–axis. The logarithmic temperature dependence for $x = 0.01$ is shown in the inset.

Typical temperature dependences of the resistivity within the conducting plane are shown in figure 1. Successive CDW transitions are clearly observed in η–Mo_4O_{11}. The metallic state is stable against doping W atoms up to 1%. As mentioned before, it couldn't obtain the single phase in the W concentration over 1% and, at the higher concentration, a phase with different crystal structure appears. The room temperature resistivity linearly increases with increasing x. If the W atoms occupy only on the tetrahedral sites [3], the in–plane resistivity should not be so affected by the doping. Moreover, the Pauli paramagnetic susceptibility slightly decreases with increasing x. η–Mo_4O_{11} is considered to have a nearly compensated FS. If W atoms substitute one of three different oxidization states of MoO_6 octahedra, they may reduce the carrier compensation.

Both $T_{\mathrm{CDW-I}}$ and $T_{\mathrm{CDW-II}}$ were dependent on the W concentration, as shown in figure 2. $T_{\mathrm{CDW-I}}$ is weakly depressed and the critical features both in the resistivity and in the magnetic susceptibility become smearing with increasing x. Hence, $T_{\mathrm{CDW-II}}$ easily disappears by doping a small amount of W atoms (less than 0.2%/Mo). The single crystal X–ray diffraction measurements support these results. When W atoms are doped, the satellite reflections belonging to the CDW–II modulation become invisible. On the contrary, the modulation of CDW–I state do not show remarkable change within the experimental accuracy, while the measured $T_{\mathrm{CDW-I}}$ is slightly depressed (see the crosses in the figure). The decrease of the Pauli paramagnetic susceptibility suggests a decrease of density of states at FS, which must lead the suppression of transition temperature. In several impurified CDW materials, the decrease of transition temperature associated with the smearing of the critical features has been observed. It is considered to be due to the local charge–density oscillation induced by the impurity [4]. These combined effects give rise to the weak suppression of $T_{\mathrm{CDW-I}}$. Additionally, since the CDW–II state has an inter–layer component of its modulated structure [2], the impurity substituted on the inter–layer sites possibly reduce the three–dimensional coherence between the intra–layer CDWs, which should give rise to the strong suppression of $T_{\mathrm{CDW-II}}$.

Below 10K, the resistivity follows "*log T*" dependence (see the inset of the figure 1). In this regime, neither the SdH nor the AMRO could be observed in contrast with the non–doped case [5,6]. This result suggests that the carriers are scattered by the impurity before making a closed orbit in the FS. It is consistent with the weak localization picture at low temperatu
hav
the
did
exp
the

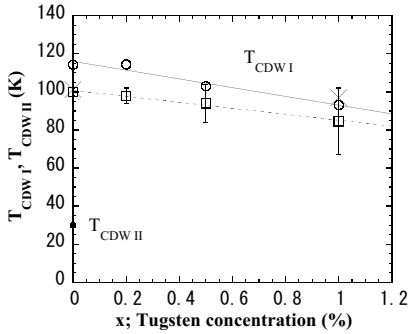

Fig. 2. CDW transition temperatures of the η–$(Mo_{1-x}, W_x)_4O_{11}$ system as a function of x. Open circles and open squares indicate the CDW–I transition temperature measured by the magnetic susceptibility and the resistivity, respectively. The large crosses are obtained by the measurements of X–ray satellite reflection intensity.

References

[1] E. Canadell *et. al*, J. Inorg. Chem. **28** (1989) 213.

[2] Y. Nogami, *et. al*, Synth. Met. **120** (2001) 1049.

[3] H. Gruber, *et. al*, Phys. Stat. Sol. **86** (1984) 749.

[4] H. Mutka, *"Advances in the crystallographic and microstructural analysis of charge density wave"*, Kluwer Academic Publishers. pp153–184

[5] S. Hill, et. al, Phys. Rev. B**55** (1997) 2018.

[6] K. Oshima, *et. al*, proceedings in LT23.