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AUTHOR(S):

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Itinerant electron magnetism of η -carbides $\text{Co}_6\text{M}_6\text{C}$ and $\text{Ni}_6\text{M}_6\text{C}$ ($\text{M} = \text{Mo}$ and W)

T. Waki^{a,*}, D. Furusawa^a, Y. Tabata^a, C. Michioka^b, K. Yoshimura^b, A. Kondo^c, K. Kindo^c, H. Nakamura^a

^a*Department of Materials Science and Engineering, Kyoto University, Kyoto 606-8501, Japan*

^b*Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan*

^c*The Institute for Solid State Physics, The University of Tokyo, Kashiwa 277-8581, Japan*

Abstract

Magnetic, transport, and thermal properties of metallic η -carbides $\text{Co}_6\text{M}_6\text{C}$ and $\text{Ni}_6\text{M}_6\text{C}$ ($\text{M} = \text{Mo}$ and W) with the cubic $\text{Ni}_6\text{Mo}_6\text{C}$ -type structure have been characterized. The Ni-based compounds $\text{Ni}_6\text{Mo}_6\text{C}$ and $\text{Ni}_6\text{W}_6\text{C}$ are Pauli paramagnets with temperature-independent susceptibilities. Susceptibilities of the Co-based compounds $\text{Co}_6\text{Mo}_6\text{C}$ and $\text{Co}_6\text{W}_6\text{C}$ are enhanced and temperature-dependent. $\text{Co}_6\text{Mo}_6\text{C}$ remains paramagnetic down to the lowest temperature, while $\text{Co}_6\text{W}_6\text{C}$ undergoes an antiferromagnetic-type transition at 46 K. A metamagnetic transition was observed for $\text{Co}_6\text{W}_6\text{C}$ at 20–30 T at the lowest temperatures. The correlation among the enhancements in the susceptibility, the resistivity, and the electronic specific heat suggests the presence of moderate electron correlation in these compounds.

Keywords: transition metal alloys and compounds, solid state reaction, electrical transport, heat capacity, magnetisation, high magnetic fields, magnetic measurements

*Corresponding author

Email address: waki.takeshi.5c@kyoto-u.ac.jp (T. Waki)

1. Introduction

Cubic η -carbide-type transition-metal bimetallic compounds T_3M_3X (prototype Fe_3W_3C ; denoted as η -6) and T_6M_6X (Ni_6Mo_6C ; η -12), where T stands for a $3d$ transition metal, M a $4d$ or $5d$ transition metal in group 4–6, and $X = C, N$, or O , have been studied for about half a century because of their hardness [1, 2] and potential catalytic ability [3]. However their detailed electronic properties remain to be investigated. Recently, a wide variety of magnetic properties of η -6 have been reported by our group [4, 5, 6, 7] and others [8, 9, 10, 11, 12, 13, 14]. For example, we have found that Fe_3Mo_3N show a non-Fermi-liquid behavior at low temperatures [4], and proposed that, in Fe_3Mo_3N , long-range magnetic order is suppressed by the geometric frustration inherent to the η -carbide structure in spite of strong magnetic correlation [5]. Interesting magnetism is also expected in η -12, since η -6 and η -12 are different only in the occupation site of X atoms. In this article, we report briefly low-temperature physical properties of Co- and Ni-based η -12, Co_6Mo_6C , Co_6W_6C , Ni_6Mo_6C , and Ni_6W_6C . The result of an Fe-based η -12, Fe_6W_6C , will be published elsewhere.

2. Experiments

Polycrystalline samples of η -12, Co_6Mo_6C , Co_6W_6C , Ni_6Mo_6C , and Ni_6W_6C , were obtained by solid-state reactions from powdered raw materials. For the Mo-based compounds, a mixture of the $3d$ element, Mo, and C was sealed in an evacuated silica tube and heated in a muffle furnace at $1000^\circ C$ for 48 h. The synthesis of the W-based compounds was started from a mixture of the $3d$ element, W, and W_2C , and followed by the same procedures. The obtained samples were characterized by X-ray diffraction analysis to have the cubic Ni_6Mo_6C -type structure (space group $Fd\bar{3}m$). Estimated lattice constants at room temperature are $10.903(1)$, $10.905(1)$, $10.894(3)$, and $10.896(2)$ Å for Co_6Mo_6C , Co_6W_6C , Ni_6Mo_6C , and Ni_6W_6C , respectively; these values are in good agreement with those reported in literatures [15, 16, 17, 18, 19, 20]. Temperature and field dependences of the magnetization in the range from 2 to 300 K and up to 7 T were measured using a SQUID magnetometer, MPMS (Quantum Design), installed at the Research Center for Low Temperature and Materials Sciences, Kyoto University. Temperature dependences of the resistivity were measured for pellets sintered from powder by the four-probe method down to 5 K. Specific heat measurements were performed using a

Figure 1: (Color online) Temperature dependences of the susceptibility for η -12.

PPMS (Quantum Design). High-field magnetization measurements up to 54 T were performed with a pulse magnet equipped at ISSP, the University of Tokyo.

3. Results and discussion

3.1. Magnetic susceptibility

Figure 1 shows temperature dependences of the susceptibility $\chi(T)$ for η -12 measured under an external field of 0.1 T. The susceptibility of $\text{Co}_6\text{Mo}_6\text{C}$ has a Curie-Weiss-type temperature dependent term together with a temperature independent contribution. No indication of magnetic order was found down to 2 K. We fitted the data between 100 and 300 K to a modified Curie-Weiss function $\chi(T) = C_C/(T-\theta) + \chi_0$, where C_C is the Curie constant, θ the

Table 1: Characteristic values of η -12. A : the coefficient of the T^2 term of the resistivity, γ : the electronic specific heat coefficient, Θ_D : the Debye temperature, GS: the magnetic ground state (AF and P represent antiferromagnetic and paramagnetic, respectively), and T_N : the Néel temperature.

	$A \times 10^9$ ($\Omega\text{cm}/\text{K}^2$)	$\gamma \times 10^3$ ($\text{J}/\text{mol K}^2$)	Θ_D (K)	GS	T_N (K)
$\text{Ni}_6\text{W}_6\text{C}$	1.9	37.4	407	P	-
$\text{Ni}_6\text{Mo}_6\text{C}$	12	82.9	504	P	-
$\text{Co}_6\text{W}_6\text{C}$	-	87.3	402	AF	46
$\text{Co}_6\text{Mo}_6\text{C}$	33	113.3	481	P	-

Weiss temperature, and χ_0 a temperature-independent term, and obtained the effective paramagnetic moment $p_{\text{eff}} = 0.99 \mu_B/\text{Co}$, $\theta = -73.3$ K, and $\chi_0 = 3.40 \times 10^{-3}$ emu/mol. For the corresponding η -6, $\text{Co}_3\text{Mo}_3\text{C}$, we have observed a different temperature dependence, namely a broad hump at ~ 120 K [6], which is characteristic of the exchange-enhanced Pauli paramagnet undergoing an itinerant electron metamagnetic transition. This fact suggests that the C sublattice plays an important role in determining the magnetism.

$\text{Co}_6\text{W}_6\text{C}$ shows a similar temperature dependent susceptibility at high temperatures. The fit of the data between 100 and 300 K to the modified Curie-Weiss function yields $p_{\text{eff}} = 1.13 \mu_B/\text{Co}$, $\theta = -93.4$ K, and $\chi_0 = 2.82 \times 10^{-3}$ emu/mol. The obtained values are comparable to those of $\text{Co}_6\text{Mo}_6\text{C}$, suggesting a similar electronic state at high temperatures. A cusp was observed at $T_N \simeq 46$ K, indicating the presence of a magnetic transition, probably of antiferromagnetic type.

Susceptibilities for $\text{Ni}_6\text{Mo}_6\text{C}$ and $\text{Ni}_6\text{W}_6\text{C}$ are small and nearly temperature independent, suggesting no significant magnetic enhancement in these compounds. In other words, these compounds are simple Pauli paramagnets. The susceptibility of $\text{Ni}_6\text{Mo}_6\text{C}$ is slightly larger than that of $\text{Ni}_6\text{W}_6\text{C}$ except below ~ 15 K, where $\text{Ni}_6\text{Mo}_6\text{C}$ shows a marked upturn. The low-temperature upturn is probably ascribed to paramagnetic impurities.

3.2. Resistivity

Figure 2 illustrates temperature dependences of the resistivity $\rho(T)$. All the compounds show metallic behaviors with positive temperature coefficients. Residual resistivities $\rho(0)$ are relatively large in the range of 0.05–0.3

Figure 2: (Color online) Temperature dependences of the resistivity for paramagnetic η -12. Residual resistivities were subtracted. In the inset, the resistivity of antiferromagnetic $\text{Co}_6\text{W}_6\text{C}$, normalized by the value at 300 K, is compared with that of paramagnetic $\text{Co}_6\text{Mo}_6\text{C}$.

$\text{m}\Omega\text{cm}$ because the measurements were performed for sintered pellets, resulting in large errors in the absolute values. The main panel of Fig. 2 shows data of the paramagnetic compounds, where residual resistivities were subtracted to highlight temperature dependences. The temperature variation becomes larger in the order of $\text{Ni}_6\text{W}_6\text{C}$, $\text{Ni}_6\text{Mo}_6\text{C}$, and $\text{Co}_6\text{Mo}_6\text{C}$. At high temperatures, all the curves are not linear but convex upward, suggesting the effect of magnetic fluctuations [21]. At low temperatures, all the three compounds show Fermi-liquid-type quadratic temperature dependences as $\rho(T) = \rho(0) + AT^2$, where A is a coefficient reflecting the electron correlation. Values of A estimated from the data below 15 K are listed in Table 1.

In the inset of Fig. 2, the resistivity of magnetically ordered $\text{Co}_6\text{W}_6\text{C}$ is

plotted and compared with that of the paramagnetic counterpart, $\text{Co}_6\text{Mo}_6\text{C}$. Here the resistivity was normalized by the value at room temperature. At high temperatures, both the compounds show similar temperature dependences just as in the case of the susceptibility. It is clearly seen that the resistivity of magnetically ordered $\text{Co}_6\text{W}_6\text{C}$ deviates downward in a low-temperature region. Although we have observed no appreciable anomaly just at the expected transition temperature, $T_N = 46$ K, this behavior suggests that the magnetic scattering is reduced associated with the development of magnetic correlation, which is already started from a temperature higher than T_N .

3.3. Specific heat

Figure 3 shows C/T (C : specific heat, T : temperature) plotted against T^2 . In contrast to the $-\log T$ divergence observed for $\text{Fe}_3\text{Mo}_3\text{N}$ [4], all present η -12 show Fermi-liquid-type temperature dependences $C/T = \gamma + \beta T^2$, where γ is the electronic specific heat coefficient and β a fitting parameter. Obtained values of γ are listed in Table 1. They are larger than that expected for a simple metal, suggesting moderate electron correlation in these η -12.

The correlation among the enhancements in χ , A , and γ is noticeable for the paramagnetic compounds. According to band calculations for nonmagnetic $\text{Co}_6\text{W}_6\text{C}$ [23], the density of states at the Fermi level $D(E_F)$ is dominated by pronounced Co-3d and relatively broad W-5d components. The Co-3d partial density of states has a peak below the Fermi energy. Based on the rigid band picture, the increase in the number of electrons in the 3d bands results in the reduction of $D(E_F)$. This explains the less magnetic enhancement in the Ni-based compounds. On the other hand, it seems to be difficult to find a reliable argument to explain the M-site dependence of the magnetism.

As seen in the inset of Fig. 3, the specific heat of $\text{Co}_6\text{W}_6\text{C}$ shows a visible anomaly at $T_N = 46$ K in agreement with the $\chi(T)$ data, supporting the occurrence of a magnetic transition. Even in the magnetically ordered state, the low-temperature γ value is comparable to that of non-ordered $\text{Co}_6\text{Mo}_6\text{C}$, suggesting that most of the spin degree of freedom remains even below T_N .

Debye temperatures Θ_D converted from β using

$$\beta = \frac{12}{5}\pi^4 N k_B \Theta_D^{-3}, \quad (1)$$

Figure 3: (Color online) C/T vs. T^2 for η -12. The inset is the temperature dependence of C_p/T for antiferromagnetic $\text{Co}_6\text{W}_6\text{C}$. The arrow represents the temperature where $\chi(T)$ shows an anomaly.

where N is the number of atoms in the system and k_B the Boltzmann constant, are listed in Table 1. The values of Θ_D for the Mo-based η -12 (~ 500 K) are comparable to that of WC, 493 K [22]. The W-based η -12 have smaller Θ_D (~ 400 K). The fact that the Debye temperature is independent of the 3d element but dependent on the M element suggests that the hybridization of 4d or 5d bands with C 2p bands plays an important role in determining mechanical properties.

3.4. High field magnetization

Figure 4 shows field dependences of the magnetization M and its field coefficient dM/dH measured for antiferromagnetic $\text{Co}_6\text{W}_6\text{C}$ at 4.2 K and up to 54 T. The magnetization of paramagnetic $\text{Co}_6\text{Mo}_6\text{C}$ is also included in

the figure for comparison. The magnetization of $\text{Co}_6\text{Mo}_6\text{C}$ is nearly linear in contrast to the η -6 counterpart, $\text{Co}_3\text{Mo}_3\text{C}$, in which an itinerant electron metamagnetic transition was observed at ~ 30 T [6]. Generally, the material which shows a hump in $\chi(T)$ shows an itinerant electron metamagnetism and *vice versa* [24, 25]. This trend is confirmed in the present Co-Mo η -6 and η -12 too.

In the field-increasing process, the magnetization of $\text{Co}_6\text{W}_6\text{C}$ increases nearly linearly at low fields and jumps at $H_H \simeq 30$ T. In the field-decreasing process, the magnetization drops at $H_L \simeq 20$ T, resulting in a large hysteresis. The gradient is almost the same below and above the transition, and nearly identical to that of $\text{Co}_6\text{Mo}_6\text{C}$. In the field increasing process, as seen well in dM/dH , the transition is considerably broadened and, furthermore, looks triggered at around H_L . In other words, there may be two critical fields in the field increasing process.

Temperature dependences of the critical fields, H_H and H_L , are shown in Fig. 5. At low temperatures, H_H and H_L are clearly different, but they tend to merge with increasing temperature and coincide at a temperature of ~ 30 K much lower than T_N . This fact also suggests that the observation of two critical fields, H_H and H_L , are not due to a simple field hysteresis but to the presence of two phase transitions in the field increasing process, namely the presence of an intermediate phase. Above 30 K, the transition field decreases monotonically to zero at $\sim T_N$. The origin of this characteristic phase diagram remains to be explained, but may be related with the fact that there are two inequivalent Co sites (16d and 32e) in the η -carbide-type structure. Two anomalies in the magnetization process have actually been observed in other η -carbide-type compounds such as $\text{Fe}_3\text{Mo}_3\text{N}$ [5] and $\text{Fe}_3\text{W}_3\text{N}$ [7].

The inset of Fig. 4 shows the Arrott plot (M^2 -vs- H/M plot) of $\text{Co}_6\text{W}_6\text{C}$ at 4.2 K. The high-field part is linear, and its intercept at the vertical axis is clearly negative, indicating no intrinsic spin polarization even above the critical field. This fact suggests that the metamagnetic transition is not of the itinerant electron metamagnetism as observed in the η -6 analogue, $\text{Co}_3\text{Mo}_3\text{C}$, but a change in the magnetic structure, for example, melting of a spin-density-wave (SDW) state to a paramagnetic state or a change in the propagation vector to a different antiferromagnetic state. A similar observation has been reported for a SDW compound, NbFe_2 [26].

Figure 4: (Color online) Field dependences of the magnetization M and its field coefficient dM/dH of $\text{Co}_6\text{Mo}_6\text{C}$ at 4.2 K. The magnetization curve of $\text{Co}_6\text{W}_6\text{C}$ (broken curve) is also shown. The inset shows the Arrott plot of $\text{Co}_6\text{W}_6\text{C}$ at 4.2 K.

4. Summary

We have measured low-temperature physical properties of $\text{Co}_6\text{M}_6\text{C}$ and $\text{Ni}_6\text{M}_6\text{C}$ ($\text{M} = \text{Mo}$ and W) with the $\text{Ni}_6\text{Mo}_6\text{C}$ -type structure. $\text{Co}_6\text{Mo}_6\text{C}$ is an enhanced Pauli paramagnet with temperature-dependent susceptibility. $\text{Co}_6\text{W}_6\text{C}$ is an itinerant electron antiferromagnet with $T_N = 46$ K. A metamagnetic transition was also observed at 20–30 T at the lowest temperature. The transition is not of intrinsic spin polarization. Magnetic susceptibilities of $\text{Ni}_6\text{Mo}_6\text{C}$ and $\text{Ni}_6\text{W}_6\text{C}$ are almost temperature independent, indicating that they are Pauli paramagnets.

Figure 5: (Color online) Temperature dependences of critical fields for $\text{Co}_6\text{W}_6\text{C}$.

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