Magnetic susceptibility of \( \eta \)-carbide-type molybdenum and tungsten carbides and nitrides

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Abstract. We synthesized a series of molybdenum and tungsten \( \eta \)-carbide-type compounds and measured their magnetic susceptibility. Although the enhancement of was observed in several compounds, apparent magnetic order was found only in Fe\(_3\)W\(_3\)N (ferromagnetic at 110 K). The broad peak in Fe\(_6\)W\(_6\)C is possibly due to antiferromagnetic order. Itinerant electron metamagnetic transitions were observed in Fe\(_3\)W\(_3\)C, Fe\(_6\)W\(_6\)C, Fe\(_6\)W\(_6\)N and Co\(_6\)W\(_6\)C. The magnetic enhancement depends on the 3\(d\) element in the order Fe > Co > Ni corresponding to DOS at the Fermi energy in \( \eta \)-12 systems, whereas no clear trend has been observed in \( \eta \)-6 systems.

1. Introduction
The \( \eta \)-carbide-type compounds with the cubic Fe\(_3\)W\(_3\)C-type crystal structure (space group \( \text{Fd} \bar{3}m \)), are known as refractory and hard materials, and recently as potential catalysts. The general formula is \( M_6^fT_6^dX^cX^a_mX^m_n \), where \( M = \text{Nb, Mo, W, Ta, } \cdots \), \( T = \text{Cr, Mn, Fe, Co, Ni, } \cdots \), \( X = \text{C, N, O, } m = 0, 2, n = 0, 1 \) and the superscripts of the metal sites represent Wyckoff positions. In the case of \( m = 2 \) and \( n = 0 \), namely \( T_3M_3X \), the structure is referred to as \( \eta \)-6 (the number denotes the ratio of metal atoms against the \( X \) atom). Similarly \( m = 0 \) and \( n = 1 \), \( T_6M_6X \) is called \( \eta \)-12. In both structures, the three dimensional \( T \) metal network consists of the 16\(d\) pyrochlore lattice nested by 32\(e\) tetrahedrons called a stella quadrangula [1], which is of interest in the viewpoint of geometrical frustration. As the \( T-T \) distance in \( \eta \)-carbide-type compounds is short of 2.5 ~ 2.6 Å, the itinerant electron magnetism is expected. Although many studies were devoted on these materials, few quantum properties have been reported so far. Recently we have found a ferromagnetic quantum critical behavior in Fe\(_3\)Mo\(_3\)N [2] and also field and impurity induced ferromagnetic orders in the compound [3]. As the ferromagnetic orders are triggered by slight perturbations, the absence of magnetic long-range order in pure Fe\(_3\)Mo\(_3\)N could be due to the geometrical frustration in the stella quadrangula lattice of the Fe sublattice [3]. We also found an itinerant electron metamagnetism (IEM) in Co\(_3\)Mo\(_3\)C [4]. Therefore, a rich variety of magnetism is expected in other \( \eta \)-carbide-type compounds. In this report we show temperature dependences of \( \chi \) measured for several molybdenum and tungsten \( \eta \)-6 and \( \eta \)-12 compounds.
2. Experiments
We synthesized polycrystalline samples of Mn₃Mo₃C, Fe₃W₃N, Fe₃W₃C, Fe₆Mo₆C, Fe₆W₆C, Fe₆W₆N, Co₆W₆C, Co₆Mo₆N, Ni₆Mo₆C, and Ni₆W₆C. Except Fe₆W₆N, the synthesis has been reported in the literature together with the crystallographic information [5, 6, 7, 8, 9, 10, 11, 12, 13]. Most carbides were obtained using a standard solid state reaction from powdered elements in evacuated silica tubes. Fe₃Mo₃C was obtained by two methods; one is the solid state reaction (#1) and the other is a topotactic method from the nitride (#2) [12]. On the other hand, the nitrides were obtained using specific methods; Co₆Mo₆N was obtained via a topotactic route from Co₃Mo₃N described in the reference [5], Fe₃W₃N was successfully synthesized using a hot isostatic pressing method starting from metal elements in N₂ high-pressure gas. Fe₆W₆N was also obtained by the same method under different pressures and temperatures. The synthesized samples were checked by the powder XRD method. Except Mn₃Mo₃C and Fe₆W₆N, we obtained single phases. As impurities, MoC and Fe₃W₃N were detected in Mn₃Mo₃C and Fe₆W₆N, respectively. The temperature dependence of magnetic susceptibility χ was measured in the temperature range from 1.8 to 300 K using a SQUID magnetometer, MPMS equipped in the LTM center, Kyoto University. High field magnetization measurements were performed using a pulse magnet equipped in ISSP, the University of Tokyo, up to 50 T at 4.2 K.

3. Results and Discussion

![Figure 1. χ for η-6.](image1)

![Figure 2. χ for η-12.](image2)

Temperature dependences of χ for η-6 and η-12 compounds are summarized in Figs. 1 and 2, respectively. The data of Fe₃Mo₃N, Co₃Mo₃C and Co₃Mo₃N are taken from our previous reports [2, 4]. Most of the systems show Curie-Weiss (CW) like temperature dependences at high temperatures, suggesting magnetic enhancement in these compounds. The CW susceptibilities were fitted to a modified CW function χ = C/(T − θ) + χ₀, where C = Npₜ effμB/3kB is the Curie constant, N the number of magnetic atoms, pₜ eff the effective moment, μB the Bohr magneton, kB the Boltzmann constant, θ the Weiss temperature, and χ₀ a temperature independent term of the susceptibility. The estimated pₜ eff and θ are summarized in Table 1.

Positive θ values often correspond the Curie temperature of the system, although negative θ values in the itinerant electron system do not necessarily mean antiferromagnetic interaction. As expected from the θ value, Fe₃W₃N undergoes ferromagnetic order at 110 K. The ratio of pₜ eff/ps = 4.8, estimated by using the saturation moment at 5 K ps = 0.76μB/Fe, is larger...
than unity, which is one of characteristics for the weak itinerant electron ferromagnet. A positive $\theta$ value was also obtained for Fe$_6$W$_6$C. However, a pronounced peak in $\chi(T)$ instead of ferromagnetic order has been observed. The magnetization at 2 K shows a sudden increase at 0.55 T suggesting a metamagnetic transition (MT). This transition is possibly of spin flip in the antiferromagnet because the critical field $H_C(T)$ decreases with increasing temperature, contrary to the increase in $H_C(T)$ generally observed for IEM of exchange-enhanced nearly ferromagnetic metals. Interestingly, Fe$_3$Mo$_3$N, with almost zero $\theta$, shows a ferromagnetic non-Fermi liquid behavior at low temperature [2]. In that sense, Fe$_3$W$_3$C deserves a study for the quantum critical magnetism because it shows almost zero $\theta$ as well.

We observed $\chi(T)$ maximum behaviors in several systems; Fe$_3$Mo$_3$N, Fe$_3$W$_3$C, Co$_3$Mo$_3$C, Fe$_3$Mo$_3$C(#1), Co$_6$W$_6$C and Fe$_6$W$_6$N. Because the $\chi(T)$ maximum has been commonly observed in exchange-enhanced itinerant electron metals showing IEM, we performed high field magnetization measurements on these materials. We have already reported the IEMs observed in exchange-enhanced itinerant electron metals showing IEM, we performed high field magnetization measurements on these materials. We have already reported the IEMs in Fe$_3$Mo$_3$N [3] and Co$_3$Mo$_3$C [4]. By pulse magnetization measurements, we observed IEM at 27.8, 27 and 26.2 T in Fe$_3$W$_3$C, Fe$_6$W$_6$N and Co$_6$W$_6$C, respectively [14, 15]. Note that the result of Fe$_6$W$_6$N is only preliminary because our Fe$_6$W$_6$N sample contains extra phases. Unfortunately we have not established synthetic conditions to get a single phase of Fe$_6$W$_6$N.

No apparent anomalies were observed in $\chi(T)$ of Mn$_3$Mo$_3$C and Co$_6$Mo$_6$C, although CW-type temperature dependences were seen. Weak temperature dependences of $\chi$ were observed for Fe$_3$Mo$_3$C(#2), Co$_3$Mo$_3$N and Co$_6$Mo$_6$N. As the magnitudes are relatively large, there should be exchange enhancements. $\chi(T)$ of Ni$_6$Mo$_6$C and Ni$_6$W$_6$C remain small suggesting simple Pauli paramagnetism in these materials.

In Fe$_3$Mo$_3$C, the difference in magnetism was observed depending on synthetic routes. $\chi(T)$ of (#1) shows Pauli paramagnetism at high temperature and a gradual increase below 250 K being different from a CW behavior. On the contrary, $\chi(T)$ of (#2) is almost temperature independent. The difference may be due to the presence of excess Fe or Mo atoms occupying the counter metallic site which depends the manufacturing method [6, 12]. We note that no metamagnetic transition was observed in Fe$_3$Mo$_3$C(#1) up to 45 T, although a $\chi(T)$ maximum was observed at 35 K. The origin of the maximum might be different from those for other materials.

Among $\eta$-12 systems, a clear correlation between the enhancement of $\chi$ and the $T$ element can be seen; with increasing the number of electrons as changing $T$ from Fe to Ni, the magnetic enhancement деceases. For $\eta$-12 systems, only few results of band calculations are available [16]. The bands of Fe$_6$W$_6$C and Co$_6$W$_6$C consist of pronounced 3$d$ bands and widely spread 5$d$ W bands whose centers of gravity locate lower and higher than the Fermi energy, respectively. When we assume the rigid band model, the contribution of 5$d$ bands at the Fermi energy increases with increasing the number of electrons, resulting in a magnetically less enhanced state. On the other hand, we have not observed an appreciable trend in the magnetism among $\eta$-6 systems, although the magnetism depends sensitively on the elements at the $M$ and $T$ sites. Band structures of Fe$_3$W$_3$C and Co$_3$W$_3$C (this compound is metastable at room temperature [7]), reported in the literature, do not show marked difference from those of $\eta$-12.

4. Conclusion
We measured temperature dependences of the susceptibility for several molybdenum and tungsten $\eta$-carbide-type compounds and found some magnetically enhanced materials. An apparent magnetic long-range order was observed only in Fe$_3$W$_3$C (ferromagnetic long range order at 110 K). Fe$_3$W$_6$C is possibly antiferromagnetic. $\chi(T)$ maximum behaviors, which remind us IEM, were observed in several systems. We have found IEM in Fe$_3$W$_3$C, Fe$_6$W$_6$N and Co$_6$W$_6$C.
Table 1. Magnetic properties of η-carbide-type compounds

| materials          | $p_{\text{eff}}$ ($\mu_\text{B}/3\text{d-atom}$) | $\theta$ (K) | memo               |
|--------------------|-----------------------------------------------|--------------|--------------------|
| Mn$_3$Mo$_3$C      | 0.98                                          | -65          | CW                 |
| Fe$_3$Mo$_3$C (#1) | -                                             | -            | $\chi(T)$ max @ 35 K |
| Fe$_3$Mo$_3$C (#2) | -                                             | -            | Pauli paramagnetic |
| Fe$_3$Mo$_3$N      | 2.14                                          | 2            | $\chi(T)$ max @ 78 K, IEM @ 13.9 T |
| Fe$_3$W$_3$C       | 0.85                                          | -1           | $\chi(T)$ max @ 75 K, IEM @ 27.8 T |
| Fe$_3$W$_3$N       | 3.39                                          | 110          | F @ 110 K          |
| Co$_3$Mo$_3$C      | 2.50                                          | -124         | $\chi(T)$ max @ 90 K, IEM @ 37 T |
| Co$_3$Mo$_3$N      | -                                             | -            | Pauli paramagnetic |
| Fe$_6$W$_6$C       | 1.50                                          | 28           | $\chi(T)$ max @ 20 K, MT @ 0.55 T |
| Fe$_6$W$_6$N       | 2.74                                          | -21          | $\chi(T)$ max @ 80 K, IEM @ 27 T |
| Co$_6$W$_6$C       | 1.13                                          | -93          | $\chi(T)$ max @ 46 K, IEM @ 26.2 T |
| Co$_6$Mo$_6$C      | 0.99                                          | -73          | CW                 |
| Co$_6$Mo$_6$N      | -                                             | -            | Pauli paramagnetic |
| Ni$_6$Mo$_6$C      | -                                             | -            | Pauli paramagnetic |
| Ni$_6$W$_6$C       | -                                             | -            | Pauli paramagnetic |

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