Metamagnetism of $\eta$-carbide-type transition-metal carbides and nitrides

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Abstract. $\eta$-carbide-type transition-metal compounds include the frustrated stella quadrangula lattice. Due to characteristics of the lattice, we expect subtle transitions between frustrated and non-frustrated states. Here, we report metamagnetic transitions newly found in $\eta$-carbide-type compounds Fe$_3$W$_3$C, Fe$_6$W$_6$C and Co$_6$W$_6$C.

1. Introduction

Transition-metal nitrides and carbides with the cubic $\eta$-carbide-type structure (prototype Fe$_3$W$_3$C) are expected to show new and various electronic phenomena, because they are typical intermetallic compounds with narrow $d$-electron bands sitting at around the Fermi level [1]. However, despite that a huge number of the compounds are known to exist, their electronic properties have been less studied in contrast to extensive investigations in material science, for example, as hard and refractory materials, and as potential catalysts [2]. In the $\eta$-carbide-type structure, one can find a geometrically frustrated sublattice called the stella quadrangula lattice (16d and 32e sites in the space group $Fd\bar{3}m$; figure 1, center) [3]. This lattice is obtained by inserting a small regular tetrahedron into each tetrahedron in the pyrochlore lattice (figure 1, left). However, the nature of the frustration is essentially different from the pyrochlore lattice. The element of this lattice, which is referred to as a stella quadrangula (stellate tetrahedron; figure 1, right), is two nested regular tetrahedrons having the same center of gravity. There are two types of near-neighbor bonds, 16d–32e and 32e–32e. When considering only $J_1$ and $J_2$ corresponding to these bonds, respectively, it is found that (i) the frustration presents only when $J_2$ is negative and dominant, (ii) $J_1$ works to release the frustration, and (iii) these features do not depend on the sign of $J_1$. As a result, the frustrated and non-frustrated states are switched depending on the ratio of $J_2/|J_1|$ [4]. Thus we expect rich variety of magnetic states, and various types of transitions between frustrated and non-frustrated states associated with the variation in the $J_2/|J_1|$ ratio.

Recently, we have studied systematically electronic properties of the $\eta$-carbide-type compounds, and already reported several examples of interesting discoveries [4, 5, 6, 7]. In this paper, we focus on the metamagnetism. As summarized in figure 2, we have already

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reported a quite sharp metamagnetic transition at \( \sim 14 \) T [4] from a non-Fermi liquid ground state in Fe\(_3\)Mo_3N [5], and a rather gradual itinerant-electron metamagnetic transition in Co\(_3\)Mo\(_3\)C at \( \sim 37 \) T [6]. In the figure, data of related materials Fe\(_3\)Mo\(_3\)C and Co\(_3\)Mo\(_3\)N, which show no metamagnetic transition, are also included. The magnetism of Fe\(_3\)Mo\(_3\)C is less enhanced, resulting in the small susceptibility and no metamagnetic transition. On the other hand, in the Co systems, although the low-field susceptibilities of Co\(_3\)Mo\(_3\)C and Co\(_3\)Mo\(_3\)N are comparable, only Co\(_3\)Mo\(_3\)C shows a metamagnetic transition. We ascribed this difference to two different type of criticality, only one of which leads to the susceptibility peak and the itinerant metamagnetism [6]. These behaviors of magnetization curves are quite contrastive depending on not only the transition-metal element but also the interstitial atoms (C and N), suggesting the presence of competing interactions in the frustrated stella quadrangula lattice. In this paper, we show metamagnetic transitions newly found in other \( \eta \)-carbide-type compounds Fe\(_3\)W\(_3\)C, Co\(_6\)W\(_6\)C and Fe\(_6\)W\(_6\)C.

2. Experimental procedures

Polycrystalline samples of Fe\(_3\)W\(_3\)C, Fe\(_6\)W\(_6\)C and Co\(_6\)W\(_6\)C were synthesized by standard solid-state reactions from powdered pure elements in evacuated silica tubes [8]. The magnetization at low fields was measured by using a SQUID magnetometer, MPMS (Quantum Design) equipped in the LTM centre, Kyoto University. The high-field magnetization up to 45 T was measured by using a pulse magnet equipped in ISSP, the University of Tokyo at 4.2 K.

3. Results

3.1. Fe\(_3\)W\(_3\)C

Fe\(_3\)W\(_3\)C is known as the prototype of the \( \eta \)-carbide, which was originally found as an impurity phase in steel [9]. Magnetic properties of Fe\(_3\)W\(_3\)C have not been reported so far, although electronic structure calculations have been performed recently [10, 11, 12]. We have measured the temperature dependence of the susceptibility, which obeys the Curie-Weiss law at high temperatures (the effective moment \( \mu_{\text{eff}} = 0.85 \mu_B/\text{Fe} \) and the Weiss temperature \( \theta = -1 \) K) and exhibits a broad peak at \( \sim 75 \) K [7]. This behavior looks like an aspect of the enhanced Pauli paramagnet, although the magnetic ground state has not been confirmed microscopically. The magnetization curve of Fe\(_3\)W\(_3\)C at 4.2 K is shown in figure 3(a). A slight ferromagnetic
component coming from ferromagnetic impurities is seen as non-zero magnetization at zero field. A small jump of the magnetization was observed at \(\sim 27\) T, with a small field hysteresis of \(\sim 1\) T. Since this feature is similar to that of \(\text{Co}_3\text{Mo}_3\text{C}\), we speculate that this transition is a kind of itinerant-electron metamagnetism (polarization of 3d bands) from an enhanced Pauli paramagnetic state to a field-induced ferromagnetic state. However, the transition is not as simple as the typical itinerant-electron metamagnetism as in \(\text{YCo}_2\) [13]; the magnetization jumps only slightly and does not tend to saturate even at the field of 45 T. These anomalies would be ascribed to the non-uniform magnetization in the Fe sublattice with two different chemical sites, namely bands of only one of the sites may be polarized at the transition field. It is notable that locally different Fe moments, 0.75 and \(-0.11\) \(\mu_B\) at the 16\(d\) and 32\(e\) sites, respectively, have been estimated from band calculations [11].

3.2. \(\text{Fe}_6\text{W}_6\text{C}\)

\(\text{Fe}_6\text{W}_6\text{C}\) forms the \(\text{Ni}_6\text{Mo}_6\text{C}\)-type structure [14], which is another \(\eta\)-carbide-type structure. For both \(\text{Fe}_3\text{W}_3\text{C}\)- and \(\text{Ni}_6\text{Mo}_6\text{C}\)-type structures, the space group is identical of cubic \(\text{Fd\bar{3}m}\) (227). The difference is the site occupied by C; 16c in \(\text{Fe}_3\text{W}_3\text{C}\) and 8\(a\) in \(\text{Ni}_6\text{Mo}_6\text{C}\). The temperature dependence of the susceptibility of \(\text{Fe}_6\text{W}_6\text{C}\) shows a Curie-Weiss behavior at high temperatures (\(\mu_{\text{eff}} = 1.50\ \mu_B/\text{Fe}\) and \(\theta = 28\) K) and a sharp cusp at 20 K [7], which looks like of a typical antiferromagnetic transition. The positive Weiss temperature suggests the coexistence of ferromagnetic interaction. The magnetization curve of \(\text{Fe}_6\text{W}_6\text{C}\) at 2 K, shown in figure 3(b), exhibits a relatively sharp jump at a low field of 0.57 T, and a saturating tendency at higher fields. It is reasonable to ascribe this transition to a spin flip from an antiferromagnetic ground state to a field-induced ferromagnetic state, because the transition field decreases with increasing temperature in contrast to an opposite tendency generally expected for the itinerant-electron metamagnetism; such a tendency was indeed observed in the cases of \(\text{Fe}_3\text{Mo}_3\text{N}\) [4] and \(\text{Co}_3\text{Mo}_3\text{C}\) [6]. From band calculations, Fe moments, 0.58 and 0.25 \(\mu_B\), have been estimated at the 16\(d\) and 32\(e\) sites, respectively [11]. It is notable that the sum is roughly equivalent to the saturation magnetization. Naively we expect similar electronic structures for \(\text{Fe}_3\text{W}_3\text{C}\) and \(\text{Fe}_6\text{W}_6\text{C}\) because the metallic elements form the same sublattices and C-2\(p\) bands are much apart from the Fermi

![Magnetization curves](image)

**Figure 2.** Magnetization curves of \(\text{Fe}_3\text{Mo}_3\text{N}\) (cited from [4]), \(\text{Fe}_3\text{Mo}_3\text{C}\), \(\text{Co}_3\text{Mo}_3\text{N}\) (cited from [6]) and \(\text{Co}_3\text{Mo}_3\text{C}\) (cited from [6]) at 4.2 K.
level. By contrast, however, the experimental observations are qualitatively different, suggesting the delicate and competitive interactions in the Fe sublattice.

3.3. Co$_6$W$_6$C
Co$_6$W$_6$C forms the Ni$_6$Mo$_6$C-type structure [15, 16] as Fe$_6$W$_6$C, and is known as a material with extremely high bulk modulus [17]. The temperature dependence of the susceptibility is similar to that of Fe$_3$W$_3$C; the susceptibility follows the Curie-Weiss law at high temperatures ($\mu_{\text{eff}} = 1.13 \mu_B$/Co and $\theta = -93K$) and shows a broad peak at $\sim 80$ K. As expected from the broad peak in the susceptibility, we observed a metamagnetic transition as in figure 3(a) with a relatively large field hysteresis. The transition fields are 22.8 and 29.6 T at field-increasing and decreasing processes, respectively. Considering the similar behaviors of the susceptibility and the magnetization, this transition is probably classified as the itinerant-electron metamagnetism as those observed in Co$_3$Mo$_3$C and Fe$_3$W$_3$C.

4. Summary
We have shown metamagnetic transitions found in Fe$_3$W$_3$C, Fe$_6$W$_6$C and Co$_6$W$_6$C. Together with previous data, we summarize as a number of $\eta$-carbide-type compounds exhibit metamagnetic transitions, indicating that the magnetism is, in general, highly enhanced in these compounds. The transitions of Fe$_6$W$_6$C and Co$_6$W$_6$C are possibly the itinerant-electron metamagnetism as in Co$_3$Mo$_3$C. Compared with these moderate transitions, the quite sharp discontinuity of Fe$_6$Mo$_3$N from the nonmagnetic non-Fermi liquid state [4] appears to be contrastive. The origin of this transition remains for further detailed studies. The ground state of Fe$_6$W$_6$C is likely to be antiferromagnetic, which is relatively unstable against external field. The rich variety of the magnetism is probably related with competing interactions in the frustrated stella quadrangula sublattice in the $\eta$-carbide-type structures.

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