Geometric frustration in the stella quadrangula lattice and metamagnetism in Fe$_3$Mo$_3$N

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Abstract. η-carbide-type transition-metal compounds, which include the stella quadrangula lattice, are good candidates for testing the geometric frustration in the itinerant electron magnet. The broad peak observed in the temperature dependence of the susceptibility for one of the η-carbide-type bimetallic nitrides, Fe$_3$Mo$_3$N, has been confirmed microscopically by $^{95}$Mo NMR Knight-shift measurements. The itinerant electron metamagnetic transition observed in this compound is discussed in connection with the $\chi(T)$ behavior.

1. Introduction
Transition-metal nitrides and carbides with the η-carbide-type structure are expected to show new and various electronic phenomena and functions, because they are typical intermetallic compounds with narrow d-electron bands. However, despite that a huge number of the compounds have been 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 [1]. Recently, we have studied systematically electronic properties of the η-carbide-type compounds, and already reported several examples of interesting discoveries [2, 3, 4]. In this article, we briefly summarize geometrical characteristics of the η-carbide-type structure, emphasizing possible geometric frustration of the magnetic interaction in the stella quadrangula lattice found in this structure [5]. As an example of the experimental data, we show the results of NMR measured for a η-carbide-type nitride Fe$_3$Mo$_3$N, which shows quantum criticality and sharp itinerant-electron metamagnetism.

2. Geometrical characteristics of the η-carbide-type structure
The prototypes of η-carbide-type compounds are Fe$_3$W$_3$C and Ni$_6$Mo$_6$C. For both cases, the space group is cubic Fd$\overline{3}$m (227). 3d elements (Fe and Ni) occupy two crystallographic sites with the Wyckoff notations 16$d$ and 32$e$. 4d and 5d elements (Mo and W) occupy the 48$f$ site. The difference between Fe$_3$W$_3$C- and Ni$_6$Mo$_6$C-type structures is the atomic position of C. In the former, C atoms occupy the 16$c$ site but in the latter the 8$a$ site. A number of carbides and nitrides with the same structure are known to exist. The general chemical formulas can be written as (T$_2$T$'$)$_3$M$_5$X and (T$_4$T$'$)$_3$M$_8$X. When T and T$'$ sites are occupied by the same element as Fe in Fe$_3$W$_3$C, the sublattice composed of the 16$d$ and 32$e$ sites is called the stella quadrangula lattice [5], which plays an essential role in determining magnetic properties of the η-carbide-type bimetallic compounds. When a 3d element occupies the metallic sites, the narrow
Figure 1. (a) The *stella quadrangula* lattice (Wyckoff positions 16d and 32e) found in the \( \eta \)-carbide-type structures (space group \( Fd\overline{3}m \), in this figure, the origin choice 2 was selected). (b) The *stella quadrangula* as an element of the *stella quadrangula* lattice. \( J_1 \) (black bonds) and \( J_2 \) (white bonds) correspond to NN (16d–32e) and NNN (32e–32e) interactions, respectively.

d bands are likely to sit at around the Fermi level \([6]\), and dominate the magnetic properties. As a result, the \( \eta \)-carbide-type compounds behave as typical itinerant electron magnets with metallic conductivity. On the other hand, C and N atoms, with their p states far below the Fermi level, play an important role in their mechanical properties.

The *stella quadrangula* lattice is schematically shown in figure 1(a). The element of this lattice is a ‘*stella quadrangula*’ (figure 1(b)), which means a stellate (star-shaped) tetrahedron, or a tetra-capped tetrahedron. In a different viewpoint, the *stella quadrangula* can be regarded as two nested regular tetrahedrons having the same center of gravity. The *stella quadrangula* lattice is a corner-shared lattice of *stella quadrangulae* just like the pyrochlore lattice as the corner-shared tetrahedral lattice. In the *stella quadrangula*, there are two types of near-neighbor bonds, 16d–32e and 32e–32e. These nearest-neighbor (NN) and next-nearest-neighbor (NNN) distances are nearly the same, for which a direct exchange coupling is expected, while third neighbors (16d–16d) are much apart. In fact NN and NNN distances depend on the atomic coordinate of 32e (zzz), where \( z \) should be determined experimentally. In particular, when \( z = 0.3 \), the NN and NNN distances are the exactly same, and experimental values close to \( z = 0.3 \) have been reported for actual \( \eta \)-carbide-type compounds. Thus it is reasonable to consider only \( J_1 \) and \( J_2 \) corresponding to the NN and NNN interactions, respectively, and neglect those of further neighbors.

To visualize and speculate the general nature of the *stella quadrangula* lattice, it is useful to examine the two dimensional version of the *stella quadrangula*, which is a tri-capped triangle as shown in figure 2. Here we take account of only the outer edge interaction \( J_1 \) and inner triangle interaction \( J_2 \), and consider the arrangement of Ising spins. As in figure 2(a), when \( J_1 \) is negative and \( J_2 \) is zero, the elements is not frustrated (open and closed circles represent up and down spins). However, once negative \( J_2 \) comparable to \( J_1 \) is introduced, the element turns to be a typical frustrated lattice (figure 2(b)). As another possibility, when \( J_1 \) is positive and \( J_2 \) is zero, needless to say, the element is not frustrated, but the same situation occurs when negative \( J_2 \) comparable to \( J_1 \) is introduced. These facts leads to the following speculations for the *stella quadrangula*: (i) The element is frustrated only when \( J_2 \) is negative and dominant. (ii) \( J_1 \) works to release the frustration. (iii) The frustration does not depend on the sign of \( J_1 \). In other words, the frustrated and non-frustrated states are switched depending on the
circles imply up and down spins, and 'gray' circles unfixed spins. The cases (a) and (c) with
bonds represent ferromagnetic and antiferromagnetic interactions, respectively. Open and closed
We denote outer-edge and inner-triangle interactions as $J$.

Figure 2. Ising spins in a tri-capped triangle, two-dimensional version of the *stella quadrangula*. We denote outer-edge and inner-triangle interactions as $J$ and $J_2$, respectively. Open and closed circles imply up and down spins, and 'gray' circles unfixed spins. The cases (a) and (c) with

$J_2 = 0$ are not frustrated, while (b) and (d) with negative $J_2$ comparable to $J_1$ are frustrated.

ratio of $J_2/|J_1|$. The presence of the same general trends were verified for Heisenberg spins in
the infinite corner-shared network of *stella quadrangulae*, by calculating the dispersion of the
Fourier transform of the exchange integral matrix for the unit cell of the *stella quadrangula*
lattice with assuming various $J_2/J_1$ ratios [3]. In conclusion, in the $\eta$-carbide-type bimetallic
magnets, we expect subtle transitions between frustrated and non-frustrated states associated
with the variation in the $J_2/|J_1|$ ratio.

3. Susceptibility peak and metamagnetism in Fe$_3$Mo$_3$N

One of the most interesting $\eta$-carbide-type compounds is Fe$_3$Mo$_3$N, which shows a quantum
critical behavior at low temperature [2] and a quite sharp itinerant-electron metamagnetic
transition at $\sim$14 T [4]. The exchange-enhanced Pauli paramagnetism of Fe$_3$Mo$_3$N is
characterized by a broad peak in the temperature dependence of the susceptibility, observed
at $\sim$80 K [2]. Here, as a microscopic evidence of the $\chi(T)$ peak, we show the result of the
Knight shift estimated from the $^{95}$Mo NMR. A spin-echo NMR experiment was done with a
phase-coherent type spectrometer at ISSP, the University of Tokyo. Figure 3 shows an example
of Mo NMR spectrum measured at 300 K and under the external field of 10.51 T. The Mo element
has two observable isotopes; $^{95}$Mo (natural abundance 15.9%) with the nuclear spin $I = 5/2$, the
gyromagnetic ratio $\gamma = 2.774$ MHz/T and the quadrupole moment $Q = -0.12 \times 10^{-24}$ cm$^2$, and
$^{97}$Mo (9.5%) with $I = 5/2$, $\gamma = 2.832$ MHz/T and $Q = -1.1 \times 10^{-24}$ cm$^2$. Since the site symmetry of the Mo site ($48f$) is $2nm$, the asymmetric quadrupole interaction is expected
at the Mo site. As seen in figure 3, the spectrum looks with the quadrupolar satellites, but the $^{95}$Mo and $^{97}$Mo components are not resolved due to their close $\gamma$ values. Hence we take the peak position in the spectrum as the resonance frequency of the $^{95}$Mo component, and estimate the $^{95}$Mo Knight shift at various temperature between 4.2 and 300 K. The temperature
dependence of the $^{95}$Mo Knight shift thus obtained is plotted in figure 4(a) together with the
data of macroscopic susceptibility. At high temperatures, the Knight shift exactly follows the
temperature dependence of the susceptibility and takes a maximum at $\sim$80 K. Thus the presence
of the broad $\chi(T)$ peak is evidenced from a microscopic viewpoint. At low temperatures,
the Knight shift approaches a constant value, in contrast to the critical divergence of the
susceptibility. Here it should be noted that the susceptibility was measured under a relatively
low field of 1 T, while the Knight shift at $\sim$10 T. The low-temperature $\chi(T)$ upturn is ascribed
to either the essential quantum critical divergence associated with the non-Fermi liquid behavior
or the Curie term of the paramagnetic impurities. In the former case, since the quantum critical
behavior is suppressed by the high magnetic field of the order of 10 T, as evidenced in specific heat
measurements [2], no divergence in the Knight shift measured under the high field is reasonable.
In figure 4(b), the Knight shift is plotted against the susceptibility with temperature as an
Figure 3. An example of Mo NMR spectrum measured for Fe$_3$Mo$_3$N at 300 K and under the external field of 10.51 T. The broken line represents the zero Knight shift position of $^{95}$Mo.

Implicit parameter. The high-temperature linear part to the $K-\chi$ plot gives an approximate value of the hyperfine coupling $-6.0$ T/$\mu_B$, which is compared with the typical on-site hyperfine coupling constant expected for the Mo nucleus $\sim-40$ T/$\mu_B$, suggesting that the contribution of the Mo magnetism is rather minor but the Fe sublattice forming the *stella quadrangula* lattice plays a principal role in the magnetism of Fe$_3$Mo$_3$N.

In general, the $\chi(T)$ peak is closely related to the occurrence of the itinerant electron metamagnetism. Yamada developed a simple theory based on the free energy expansion of the magnetization $M$ by taking account of the effect of spin fluctuations, and succeeded in explaining itinerant electron metamagnetic transitions of various materials [7]. In the classical theory, the itinerant electron metamagnetism takes place under the conditions $a > 0$, $b < 0$, and $c > 0$ with $3/16 < ac/b^2 < 9/20$, where $a$, $b$, and $c$ are expansion coefficients given in the free-energy expansion up to the $M^6$ term as

$$F = F_0 + \frac{1}{2}aM^2 + \frac{1}{4}bM^4 + \frac{1}{6}cM^6.$$  \hspace{1cm} (1)

Yamada proposed a relation for estimating $ac/b^2$ from $\chi(T)$ as

$$\frac{ac}{b^2} = \frac{5}{28} \left[ 1 - \frac{\chi(0)}{\chi(T_{\text{max}})} \right]^{-1},$$  \hspace{1cm} (2)

where $T_{\text{max}}$ is the temperature where $\chi(T)$ takes a maximum. We apply this relation to Fe$_3$Mo$_3$N. By extrapolating the high-temperature Knight shift data to the lowest temperature and excluding the effect of the low-temperature critical divergence, intrinsic $\chi(T_{\text{max}})$ and $\chi(0)$ are estimated to be $18.2 \times 10^{-3}$ and $12.7 \times 10^{-3}$ emu/(f.u. mol), respectively. With these values, $ac/b^2$ is estimated as 0.59, which is outside the upper bound of the criterion $9/20 = 0.45$, suggesting that Yamada’s theory is too simple to explain the itinerant electron metamagnetism of Fe$_3$Mo$_3$N. One of the most plausible reasons for the discordance is that the magnetic order parameter $M$ is not uniform in this system owing to the presence of two different magnetic sites in the Fe sites. In other words, the magnetic state of this compound is determined as a result of the competition between $J_1$ and $J_2$ in the *stella quadrangula* lattice as mentioned above. In this case, the metamagnetic transition is interpreted as the field-assisted release of the frustration from
Figure 4. (a) The temperature dependence of the $^{95}$Mo Knight shift measured for Fe$_3$Mo$_3$N. The susceptibility (solid curve) is also shown. The Knight shift and the susceptibility were measured under the fields of 10.51 and 1 T, respectively. (b) The $K$–$\chi$ plot for $^{95}$Mo NMR. The linear relation at high temperatures (straight line) gives the hyperfine coupling constant $A_{hf} = -6.0$ T$/\mu_B$.

the frustration-induced non-ordered ground state. A similar discordance between experimental result and Yamada’s theory has already been reported for another $\eta$-carbide-type bimetallic compound Co$_3$Mo$_3$C [3].

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