Phase transition in the normal state of the non-centrosymmetric superconductor Mo$_3$Al$_2$C

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Abstract. We found a phase transition in the normal state of superconducting carbide, Mo$_3$Al$_2$C by nuclear magnetic resonance (NMR) measurement. At $\sim$130 K the sharp central NMR line broadens and has additional broad components at the foot. In addition, the Knight shift and the spin-lattice relaxation rate exhibit a significant decrease, suggesting the reduction in the conduction electron density. From these results, Mo$_3$Al$_2$C undergoes the phase transition which can be understood as the charge-density wave ordering. The decrease in $1/T_1$ confirms the superconductivity appears in the partially quenched Fermi surface.

1. Introduction
The cubic $\beta$-Mn type (space group $P4_132$) crystal structure is unique. The Mn-II (12$d$) sites construct a corner sharing regular triangular network, where antiferromagnetic interaction between moments at 12$d$ site would give rise to geometrical frustration[1]. Then the lack of long-range magnetic ordering in pure $\beta$-Mn is interpreted as this effect in the $\beta$-Mn lattice. Looking from another point of view, this structure does not possess a center of inversion. In superconducting materials with an inversion center, the Cooper pairs are either in the spin-singlet state or in the spin-triplet state due to the Pauli exclusion principle and parity conservation. However, when the inversion symmetry is broken, the absence of inversion symmetry along with parity-violating antisymmetric spin-orbit coupling allows admixture of spin-singlet and spin-triplet components. The extent of parity mixing depends on the strength of the spin-orbit coupling that is enhanced by the lack of inversion symmetry. In such materials, novel superconducting properties can be expected.

A metallic carbide, Mo$_3$Al$_2$C, crystallizing a $\beta$-Mn type crystal structure exhibits the superconductivity (SC) at $T_c$=9 K[2]. Recently, Bauer et al. and Karki et al. independently investigated the normal and superconducting state properties in polycrystalline sample of Mo$_3$Al$_2$C[3, 4]. It was reported that Mo$_3$Al$_2$C shows temperature-independent Pauli paramagnetic behavior in the magnetic susceptibility and no phase transition in the normal state[4]. The Sommerfeld constant is estimated to be $\gamma \approx$18 mJ/mol K$^2$. The electronic specific heat jump at the transition point $\Delta/\gamma T_c \approx 2.2$ suggests the strong-coupling SC. The notable features of this compound are power-law behaviors of the specific heat and the nuclear spin-lattice relaxation rate $1/T_1$ in the superconducting state, implying that the order parameter is not of conventional s-wave. In this paper, we reported the first observation of the phase
2. Experimental
Polycrystalline samples of Mo$_3$Al$_2$C were arc-melted under an argon atmosphere as described in detail elsewhere[4]. NMR experiment was carried out using a conventional phase-coherent pulsed spectrometer.

3. Result and discussions
We have performed $^{27}$Al NMR experiment. Al atoms in Mo$_3$Al$_2$C are located at Mn-I (8c) site in the $\beta$-Mn type structure. Figure 1 (a) and (b) show field-swept NMR spectra at fixed frequency of 83.5 MHz. The spectrum at 200 K is sharp and symmetric, indicating that quadrupole interaction is negligible. On the other hand, the spectrum at 80 K has broad components at the foot of the intense peak. The width of the broad components is independent of the magnetic field, suggesting that these components originate from the appearance of quadrupole satellite lines due to the enhancement of quadrupole interaction at low temperatures. To see the temperature evolution in the sharp peak, we show, in Fig. 2, the NMR spectra obtained from fast-Fourier transformation (FFT) technique at a constant magnetic field of $H=7.503$ T. Above 180 K, the spectrum is a symmetric Lorentzian-type line shape. With decreasing temperature, a broad component develops at the foot of the sharp peak. The full width at half maximum of the spectra below 100 K is six times larger than that above 200 K.

The inset of Fig. 2 shows the temperature dependence of the Knight shift $K$ measured at the central peaks of the $^{27}$Al NMR spectrum. $K$ takes positive values which is smaller than that of Al metal (0.16 %) in all temperatures. $K$ decreases with temperature followed by almost temperature-independent behavior below 100 K. The change in $K$ between 170 and 100 K

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**Figure 1.** (a), (b) $^{27}$Al NMR spectra obtained by sweeping magnetic field at fixed frequency of 83.5 MHz.

**Figure 2.** (Color on line) Temperature variation of the central line of $^{27}$Al NMR spectra. Data were obtained by fast-Fourier-transformation technique at a fixed magnetic field. Inset shows the temperature dependence of $^{27}$Al Knight shift.
implies the electronic structure modifications. For the nonmagnetic materials, the total $K$ can be written as,

$$K = K_s + K_{\text{dia}} + K_{\text{orb}},$$  

(1)

where $K_s$, $K_{\text{dia}}$, and $K_{\text{orb}}$ are the Fermi-contact, the orbital, and the diamagnetic terms, respectively\[^5\]. Using the density of states at Fermi level $D(E_F)$, the sum of the first two terms can be expressed by

$$K = K_s + K_{\text{dia}} = \left\{ \frac{H_s}{N\mu_B} - \frac{8\pi}{9}\left(\frac{m^*}{m}\right)^2 \right\}\chi_P \propto D(E_F),$$  

(2)

where $H_s, N, \mu_B, m^*/m$, and $\chi_P$ are the Fermi contact hyperfine field, Avogadro’s number, the Bohr magneton, the band effective mass ratio, and the Pauli paramagnetic susceptibility, respectively. By considering that $K_{\text{orb}}$ is temperature-independent, the drop of $K$ can be interpreted as a decrease in $D(E_F)$.

It is well known that $1/T_1$ probes $D(E_F)$. The nuclear magnetization $M(t)$ was measured using the free-induction-decay (FID) amplitude so as to selectively obtain the $T_1$ value of the sharp line. The nuclear magnetization recovery $m(t)$, which is defined by $m(t) = [M(\infty) - M(t)]/M(\infty)$, does not follow the expected theoretical function\[^6\]. This is probably due to the distribution of $T_1$ values stemming from some impurities, such as Mo$_3$Al$_8$, MoC, and Mo. In order to extract a characteristic relaxation rate $1/T_1^*$, we fitted the recovery curves to a stretched exponential function,

$$m(t) = \exp\left[-\left(\frac{t}{T_1^*}\right)^\beta\right],$$  

(3)

where $\beta$ is the stretching exponent with $0 < \beta \leq 1$\[^7\]. As shown in Fig. 3, obtained $\beta \sim 0.7$ is nearly temperature-independent both above and below the transition temperature, indicating
that the characteristic of $m(t)$ does not vary with temperature. Figure 4 shows the temperature dependence of $1/(T_1^* T)$. The present $1/(T_1^* T)$ value below 90 K is four times smaller than the earlier report[3]. The discrepancy is ascribed to the different recovery function employed to extract $1/T_1$. The remarkable feature is the rapid decrease of $1/(T_1^* T)$ at $\sim 120$ K. The values of $1/(T_1^* T)$ at low temperatures are one order smaller than those at high temperatures. Because of the relation of $1/(T_1^* T) \propto D(E_F)^2$, $D(E_F)$ at low temperatures is roughly estimated to be 30% of that at high temperature. This result demonstrates that Mo$_3$Al$_2$C exhibits the phase transition accompanying the partially quenching of Fermi surface. The decrease in $D(E_F)$ is also inferred from the $K$. By further decreasing temperature, $1/(T_1^* T)$ decreases below $T_c$, indicating SC occurred at the partially quenched Fermi surface.

We speculate that this transition is connected with the formation of the charge- density wave (CDW). The reductions in $^{27}K$ and $1/(T_1^* T)$ at the transition are ascribed to the appearance of gap at $D(E_F)$ owing to the CDW formation. The broadening and the change in NMR line shape arise via a spatial distribution of the electric-field gradient (EFG) tensor at the observed nuclear site. Since CDW transition is predominantly driven by Fermi surface nesting, such transition require low-dimensional character in crystal structure. The highly anisotropic Fermi surface is responsible for the formation of the CDW. Further band calculation and experiment using single crystalline sample is needed to clarify the transition at $\sim$130 K.

4. Conclusion
We have investigated the non-centrosymmetric Mo$_3$Al$_2$C using NMR measurement. The reduction in the conduction electron density at $\sim 130$ K is inferred from the decrease in $^{27}K$ and $1/(T_1^* T)$. In addition $^{27}$Al NMR line shape shows a sudden change owing to the distribution of EFG tensor at Al position. We thus conclude that the reduction in $D(E_F)$ is associated with the appearance of a gap at the Fermi surface resulting from a CDW transition in Mo$_3$Al$_2$C. The decrease in $1/T_1^*$ confirms the SC appears in the partially quenched Fermi surface.

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