Electron correlation in Pauli paramagnetic Cr$_2$AlC, Cr$_2$GaC and Cr$_2$GeC

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Abstract. Cr$_2$AlC, Cr$_2$GaC, and Cr$_2$GeC are classical MAX phase compounds, for which successful synthesis of bulk equilibrium phases has been reported in an early stage. Although it has been established that they are Pauli paramagnetic down to the lowest temperature, the extent of the exchange enhancement depends on the A element (A = Al, Ga, and Ge). We discuss the nature of electron correlation by analyzing low-temperature resistivity, specific heat, and susceptibility in terms of the Kadowaki-Woods and Wilson ratios.

1. Introduction

The $M_{n+1}AX_n$ (space group $P6_3/mmc$, abbreviated as MAX) phases are layered, hexagonal, carbides and nitrides, where $M$ is an early transition metal, $A$ is an A-group (mostly groups IIIA and IVA) element, and $X$ is C and/or N, and $n = 1, 2, 3, \ldots$ [1]. MAX phases have attracted considerable attention recently due to their unique material properties combining the characteristics of metals and ceramics and the presence of a large number of isostructural compounds. MAX phases are excellent electrical and thermal conductors.

When $M$ is the 3d transition metal element, only materials consisting of $M$ heavier than Cr are known to exist as equilibrium phases. The pure Cr$_2$AC ($A = $ Al, Ga, and Ge) compounds show Pauli paramagnetic behaviors down to the lowest temperature [2]. The magnetism is more exchange-enhanced in the order of Cr$_2$GeC, Cr$_2$GaC, and Cr$_2$AlC. On the other hand in Cr$_2$GaN, which is only one Cr-based nitride ever known, a magnetic phase transition, to the spin-density-wave (SDW) state, has been found at $\sim$170 K [3]. The origin of the SDW transition is interpreted in terms of possible Fermi-surface nesting in the two-dimensional-like electronic structure.

The purpose of this report is to discuss the nature of exchange-enhanced Pauli paramagnetism, i.e., electron correlation, in the Cr-based MAX phases, Cr$_2$AC ($A = $ Al, Ga, and Ge). NMR result of Cr$_2$AlC is also included to prove unambiguously no long-range magnetic order in the compound.

2. Experimental procedures

Polycrystalline samples of Cr$_2$AC ($A = $ Al, Ga, and Ge) were synthesized via solid-state reactions in evacuated quartz tubes. The detailed procedures have been described in elsewhere [2, 3]. The temperature dependence of the resistivity was measured for pellets sintered from powder by the conventional four-probe method at 5–300 K. Nuclear magnetic resonance (NMR) measurements
Figure 1. The field-swept NMR spectrum measured for Cr$_2$AlC at a frequency of 48.66 MHz and at 4.2 K. The simulated paramagnetic powder-pattern spectrum is also presented for comparison.

were performed for Cr$_2$AlC by a phase-coherent-type pulse spectrometer (Thamway, PROT II 2101MR). For the measurements, fine particles of the sample are soaked in paraffin to fix crystal axes at random. Spin-echo intensity was integrated and recorded as a function of external field to obtain the spectrum at 4.2 K. The nuclear spin-lattice relaxation time, $T_1$, was measured by the saturation-recovery method.

3. Results

The $^{27}$Al NMR spectrum of Cr$_2$AlC down to 77 K has already been reported by Lue et al. [5]. The spectrum shows a typical paramagnetic pattern. It is already no doubt that Cr$_2$AlC has no long-range magnetic ordering. Here just for confirmation, we extended the measurement down to 4.2 K. Figure 1 shows a field-swept spectrum of $^{27}$Al NMR measured at 4.2 K, which shows the typical paramagnetic powder pattern. This line shape is interpreted as follows. Nuclear parameters of $^{27}$Al nucleus are natural abundance 100%, nuclear spin $I = \frac{5}{2}$, the gyromagnetic ratio, $^{27}\gamma/2\pi = 11.093$ MHz/T, and the nuclear quadrupole moment $^{27}Q = 0.15 \times 10^{-28}$ m$^{-2}$. The Al site in the Cr$_2$AlC-type structure is crystallographically unique (2$d$) and axially symmetric (6$m$2), resulting in the nuclear quadrupole interaction with zero asymmetry parameter ($\eta = 0$). In the strong-field condition, we expect to observe two pairs of first-order quadrupolar satellites together with a center line. In the bottom of Fig. 1, the computer-generated powder pattern assuming the quadrupole frequency of 1.9 MHz and the absence of the internal field is presented. Here we neglected a possible hyperfine shift, for simplicity; the values of the Knight shift estimated from the experimental spectrum are small in accordance with those estimated at 77 K in Ref. [5] ($K_{\text{iso}} \sim -0.2\%$, $K_{\text{aniso}} \sim 0.01\%$). In this condition, the center line has a fine structure due to the second-order quadrupolar interaction. The calculated pattern agrees well with the experimental spectrum, proving unambiguously that Cr$_2$AlC has no long-range magnetic order at the temperature.

The $^{27}$Al nuclear spin-lattice relaxation time, $T_1$, was measured with use of the central transition of the spectrum. The multi-exponential recovery of the nuclear magnetization was fitted to the function expected for the $I = \frac{5}{2}$ nucleus [4]. The temperature dependence of the
Table 1. Lattice parameters $a$ and $c$, lattice volume $V$, the electronic specific heat $\gamma$, the density of states at the Fermi level $N(E_F)$ estimated from band calculations, the zero-temperature susceptibility $\chi(0)$, and the coefficient of the $T^2$ term in the low-temperature resistivity $A$ for Cr$_2$AC ($A = Al$, Ga, and Ge).

| Compound   | $a$ (Å) | $c$ (Å) | $V$ (Å$^3$) | $\gamma$ (mJ mol$^{-1}$K$^{-2}$) | $N(E_F)$ ((eV unit cell)$^{-1}$) | $\chi(0)$ ($10^{-4}$ emu/f.u.-mol) | $A$ ($10^{-3}$μΩ cm K$^{-2}$) |
|------------|---------|---------|-------------|-------------------------------|---------------------------------|-----------------------------------|-------------------------------|
| Cr$_2$AlC  | 2.862   | 12.832  | 91.023      | 17.15 [6]                     | 14.6 [6]                        | 2.75                              | 1.0                           |
| Cr$_2$GaC  | 2.898   | 12.651  | 92.011      | 20.25 [8]                     | 17.2 [8]                        | 3.59                              | 6.5                           |
| Cr$_2$GeC  | 2.961   | 12.122  | 92.038      | 26.12 [9]                     | 22.0 [9]                        | 5.50                              | 5.6                           |

Figure 2. The temperature dependence of the $^{27}$Al nuclear spin-lattice relaxation rate, $1/T_1$, measured for Cr$_2$AlC. The straight line indicates the Korringa relaxation. The data points indicated by triangles are cited from Ref. [5].

relaxation rate, $1/T_1$, down to 4.2 K is shown in Fig. 2. Our data are in good accordance with those above 77 K reported by Lue et al. [5]. The result of $1/T_1$ is in proportion to temperature down to the lowest temperature, namely, follows the Korringa law in all the temperature range, indicating that the relaxation is dominated by conduction electrons. This result also demonstrates that Cr$_2$AlC is a Pauli paramagnetic metal down to the lowest temperature.

We have also measured the Ga-NMR for Cr$_2$GaC, which was reported in Ref. [3]. Similarly to Cr$_2$AlC, Cr$_2$GaC shows a well resolved nonmagnetic spectrum, indicating that Cr$_2$GaC has no long-range magnetic order either.

Temperature dependencies of the resistivity for Cr$_2$AC ($A = Al$, Ga, and Ge) are shown in Fig. 3; the data for Cr$_2$GaC have already been published in Ref. [3]. They show monotonic and metallic temperature dependencies in agreement with previous data [8, 10, 11]. Here we make no mention of the origin of the residual resistivity, since the resistivity was measured for pellets sintered from powder. At low temperatures, the resistivity obeys the quadratic temperature dependance as $\rho = AT^2 + \rho_0$, where $A$ and $\rho_0$ are constants, indicating the presence of appreciable
Figure 3. Temperature dependencies of the resistivity for $\text{Cr}_2\text{AC}$ ($A = \text{Al, Ga, and Ge}$).

Figure 4. The relation between $\gamma$ and $\chi(0)$. $\gamma$ for $\text{Cr}_2\text{AlC}$ is the average of values reported in Refs. [6] and [7]. $\gamma$ for $\text{Cr}_2\text{GaC}$ was cited from Ref. [8]. $\gamma$ for $\text{Cr}_2\text{GeC}$ is the average of values given in Refs. [9] and [10]. The solid and broken lines indicate the Wilson ratios for heavy electron systems and normal metals, respectively.

4. Discussion
$\text{Cr}_2\text{AC}$ ($A = \text{Al, Ga, and Ge}$) show typical Pauli paramagnetic behavior without spontaneous magnetization in all temperature range. No long-range magnetic order has been confirmed microscopically in $\text{Cr}_2\text{AlC}$ and $\text{Cr}_2\text{GaC}$ from NMR experiments. The absence of internal field unambiguously excludes the possibility of antiferromagnetism, to say nothing of ferro- and ferrimagnetism. The result of neutron diffraction of bulk $\text{Cr}_2\text{AlC}$, which does not show any additional reflections at low temperature [12], is thoroughly consistent with no long-range order. The absence of a phase transition for $\text{Cr}_2\text{GeC}$ in the temperature range of 3–1500 K has already been confirmed in specific heat measurements [9].

Results of band structure calculations tell us that $\text{Cr}_2\text{AC}$ are typical metals in the sense that
Cr-3$d$ bands dominate the density of states at the Fermi level, $N(E_F)$. The systematic increase in $\chi$ from Cr$_2$AlC to Cr$_2$GeC is understood as the increase in $N(E_F)$, associated with the decrease of the 3$d$ band width. Furthermore, the increase of the dimensionality expected from the decrease in the interlayer distance may also give rise to magnetic enhancement. The comparison of the electronic specific heat coefficient, $\gamma$, (see Table 1) leads to the same discussion. The susceptibility at 0 K, $\chi(0)$, which was estimated from the extrapolation of the high-temperature susceptibility [3] to 0 K, is plotted against $\gamma$ in Fig. 4. The susceptibility and $\gamma$ are both proportional to $N(E_F)$, as $\gamma = \pi^2 k_B^2 N(E_F)/3$ and $\chi = \mu_B^2 N(E_F)$, respectively. The theoretical values of $\chi(0)/\gamma$, the so-called Wilson ratio, are also shown by the solid and broken lines for heavy electron systems and normal metals, respectively. The experimental points for Cr$_2$AC ($A = Al$, Ga, and Ge) deviate from the broken line of normal metals toward the solid line of heavy electron systems, indicating that Cr$_2$AC are not simple metals but more or less exchange-enhanced.

The resistivity were fit by the equation of $\rho = AT^2 + \rho_0$ in the temperature range of 5–35 K to estimate $A$ values, which are plotted in Fig. 5 against $\gamma^2$. The Kadowaki-Woods ratios, $A/\gamma^2$, expected for heavy electron systems and normal metals are also shown in the same figure by the solid and broken lines, respectively. The points for Cr$_2$AC ($A = Al$, Ga, and Ge) are close to the solid line, indicating that Cr$_2$AC belong to the correlated electron system. The mass enhancement of Cr$_2$GeC compared with bare $N(E_F)$ by a factor of 3, pointed out in Ref. [13], also looks reasonable.

In summary, in the Pauli paramagnetic Cr-based MAX phases, electron correlation plays an appreciable role, and the correlation is more enhanced in the order of Cr$_2$GeC, Cr$_2$GaC and Cr$_2$AlC.

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