≪연구논문≫ Journal of Korean Magnetics Society, Volume 5, Number 3, June 1995

Magnetic Properties and Structures of Rare earth-Aluminum Compounds RAl_2

Moo-hee Lee, Seung-wook Um and Tae-kyung Park
Department of Physics, Kon-Kuk University, Seoul 133-701

(Received 25 May 1995, in final form 28 June 1995)

Rare earth-aluminum intermetallic compounds RAl_2 (R ; Lu, Ce, Gd) are prepared by the arc-melt method and the magnetic properties and electronic structures are investigated by magnetic susceptibility measurements using SQUID magnetometer. The magnetic susceptibility of $LuAl_2$ is weakly temperature dependent and shows a Pauli susceptibility of 10.1×10^{-5} emu/mol, which means 3.2 states/eV/formula unit. On the other hand, the susceptibility data of $CeAl_2$ and $GdAl_2$ show a Curie-Weiss behavior for paramagnets. The magnetization data at low temperatures confirm that $CeAl_2$ undergoes an antiferromagnetic phase transition near 4 K whereas $GdAl_2$ a ferromagnetic transition at 170 K. The distinctive magnetic behaviors of RAl_2 originate from the different 4f band filling.

I. Introduction

Recent years rare-earth compounds have drawn a great deal of research interest due to a wealth of exotic magnetic phenomena. Also the rare-earth compounds have wide fields of application such as magnetic memories and opto-magnetic disks. In particular, rare-earth aluminum intermetallic compounds RAl_2 have been investigated extensively for understanding of complex magnetic structures [1-3]. This complexity originates from the distinct f band fillings and hybridization with orbitals of aluminum. Depending upon the rare-earth atoms R, RAl_2 exhibits various ground states and magnetic ordered structures. This comes from the magnetic instability of f moments.

RAl_2 has a cubic Laves-phase structure consisting of two interpenetrating fcc lattices [4]. Considering Al^{+3} ions are nonmagnetic, we conjecture that R ions are weakly interacting with metallic surroundings. Thus these systems are ideal to investigate the physical properties of R ion in solids. In RAl_2, f orbitals hybridize with aluminum 3p orbitals. Depending upon a degree of hybridization, RAl_2 displays various exotic magnetic phenomena such as mixed valences and spin fluctuations [5].

Among RAl_2, a number of systems such as $CeAl_2$ and $GdAl_2$ are magnetic metals due to the partially filled 4f bands and their hybridization with intervening aluminum orbitals. The ground states of $CeAl_2$ and $GdAl_2$ are reported to be antiferromagnetic [6] and ferromagnetic states [7], respectively. Also the dynamical behaviors and the physical properties in paramagnetic states are expected to be dominated by the 4f spin fluctuations. From the orbital picture, Ce^{+3} and Gd^{+3} ions carry the 4f moments due to the respective 1 and 7 electrons partially filling the 4f shells. On the other hand, $LuAl_2$ is expected to be a nonmagnetic metal since Lu^{+3} does not carry local moments due to the completely filled 4f bands by 14 electrons [8]. Therefore $LuAl_2$ is taken as a reference to compare the roles of 4f moments in various rare-earth aluminum compounds. Thus the motivation of this study is to understand the roles of 4f bands in rare earth-aluminum compounds by the magnetic susceptibility and magnetization measurements.

II. Experiments

RAl_2 sample is grown by the arc-melt techniques. The ingot sample is ground into a fine powder for magnetic property measurements. The magnetic susceptibility is measured by a DC

SQUID (superconducting quantum interference device) magnetometer at Korea Basic Research Center. The powder samples of 4~220 mg, depending upon magnitude of moment, are loaded into sample containers of transparent gelatine capsule for the magnetic moment measurement as a function of magnetic field and temperature. The sample container weighs ~50 mg but the background signal from the container is small and diamagnetic ; -4.35×10^{-7} emu/gram. Furthermore, it shows no evidence of paramagnetic tails at low temperatures. Nevertheless, the background signal from the container is separately measured and carefully subtracted. Since the magnetic susceptibility of $GdAl_2$ sample is huge, care should be taken to avoid SQUID coil saturation. Thus the magnetization curve, magnetic moment versus field, is scanned and then a correct sample amount and field strength are selected in a linear region of the curve. The spontaneous magnetization is measured at 5 Oe as temperature decreases. Degaussing the magnetometer by a field alternating sequence is executed before this measurement to obtain a small field of 5 Oe.

Ⅲ. Results and Discussion

The DC magnetic susceptibility data for $LuAl_2$ are shown in Fig. 1. The magnetization curve, magnetic moment versus field, of $LuAl_2$ is linear crossing the origin for a range of magnetic field −5.5~ +5.5 T. This rules out a possibility of contamination by ferromagnetic particles into the sample. Thus the magnetic susceptibility of $LuAl_2$ is measured at a fixed field of 1 T as a function of temperature.

The data are temperature independent, which indicate a metallic susceptibility. At low temperatures the data show a Curie upturn, which is due to a small amount of paramagnetic impurities. From the slope of the Curie increase, the impurity concentration is estimated to be less than 0.03 %. The temperature independent part of susceptibility is 8.0×10^{-5} emu/mol. Accounting for the diamagnetic susceptibility [9] from core-electrons -2.1×10^{-5} emu/mol, we get 10.1×10^{-5} emu/mol for the Pauli contribution to the susceptibility. From this value, the density of states at Fermi energy is deduced to be 3.2 states/eV/formula unit. The magnetic susceptibility data of $CeAl_2$ are shown in Fig. 2. The inverse susceptibility as a function of temperature, $1/\chi(T)$, is plotted in Fig. 3. The susceptibility of $CeAl_2$ follows a Curie-Weiss law with a Curie constant C of 0.671 emu. K/mol and a Curie-Weiss temperature of $\theta=-24.4$ K. Equating the Curie constant C with $N_A p^2 \mu_B{}^2/3k_B$ and $p=g_J[J(J+1)]^{1/2}$, where N_A is the Avogadro number, p the effective number of moments, μ_B the Bohr magneton, k_B the Boltzmann constant, g_J the Lande g factor, we obtain $p=2.39$, which is close to $p=2.54$ for ${}^2F_{5/2}$ of Ce^{+3}. The negative sign of the Curie-Weiss temperature θ indicates the interaction between 4f moments at Ce^{+3} is antiferromagnetic. Indeed the susceptibility deviates from the Curie-Weiss behavior as temperature decreases, and exhibits a maximum at 4 K then decreasing at lower temperatures. This behavior is a classical signature for an antiferromagnetic transition. The temperature at which the susceptibility is maximum, 4 K is identified as the Neel temperature T_N. Magnetization versus field above 4 K shows a linear increase whereas that below 4 K clearly indicates an abrupt jump of

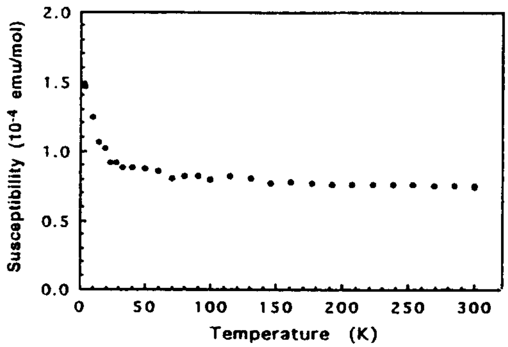

Fig. 1 The DC magnetic susceptibility of $LuAl_2$ at 1 T as a function of temperature. The core diamagnetic susceptibility is not corrected.

magnetization (Fig. 4). This kind of jump in magnetization at 2.1 K in Fig. 4 is often observed in the antiferromagnetic states and attributed to a spin-flop transition.

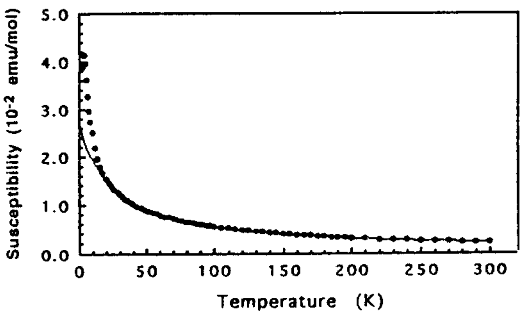

Fig. 2 The DC magnetic susceptibility of $CeAl_2$ at 1 T as a function of temperature. The core diamagnetic susceptibility is not corrected.

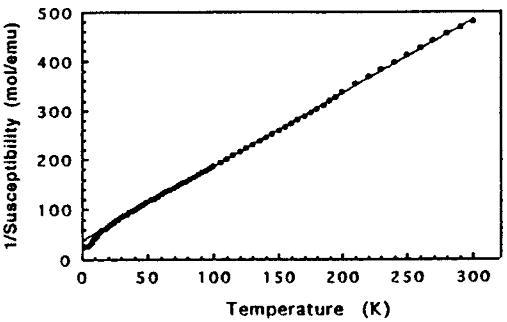

Fig. 3 The inverse susceptibility $1/x$ of $CeAl_2$ at 1 T as a function of temperature. The core diamagnetic susceptibility is not corrected.

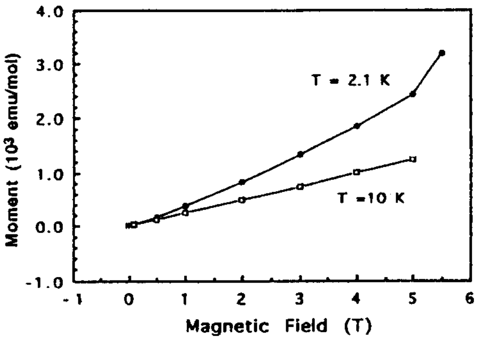

Fig. 4 The magnetization curve of $CeAl_2$ above and below the Neel temperature.

The magnetic susceptibility of $GdAl_2$ is measured at 1 kOe and shown in Fig. 5. The inverse susceptibility as a function of temperature, $1/x$ (T), is plotted in Fig. 6. The susceptibility of

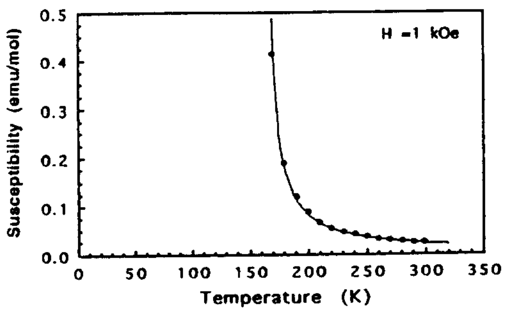

Fig. 5 The DC magnetic susceptibility of $GdAl_2$ at 1 kOe as a function of temperature. The core diamagnetic susceptibility is not corrected.

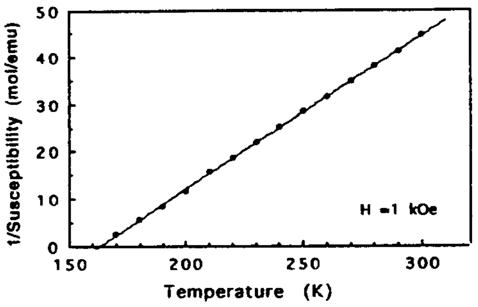

Fig. 6 The inverse susceptibility $1/x$ of $GdAl_2$ at 1 kOe as a function of temperature. The core diamagnetic susceptibility is not corrected.

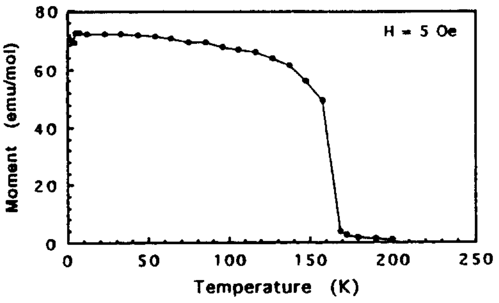

Fig. 7 The spontaneous magnetization curve of $GdAl_2$. The Curie temperature T_c is found to be 170 K.

$GdAl_2$ also follows the Curie-Weiss behavior with a Curie constant C of 3.07 emu. K /mol and a Curie-Weiss temperature of $\theta = 163$ K. From the Curie constant C we calculate $p = 5.11$, which roughly agrees with $p = 7.94$ for $^8S_{7/2}$ of Gd^{+3}. The susceptibility blows up near 170 K suggesting a magnetic transition. Indeed the magnetization measurement at lower temperatures using 5 Oe (Fig. 7) supports that the ordered state is ferromagnetic and the transition temperature is $T_c = 170$ K.

The temperature dependence of spontaneous magnetization [10] for $J = 7/2$ from the orbital picture, $^8S_{7/2}$ of Gd^{+3} is given by

$$\frac{M(T)}{M(0)} = \frac{8}{7} \coth \{ \frac{8T_cM(T)}{3TM(0)} \} - \frac{1}{7} \coth \{ \frac{T_cM(T)}{3TM(0)} \}$$

This curve is drawn and compared with data in Fig. 8. The discrepancy between the curve and data points seems to be due to undercooling of sample while the magnetic moment is measured as temperature decreases. From the magnetization curve in the ferromagnetic state, Fig. 9, the saturated magnetization is measured to be 1.5×10^4 emu /mol. Since the lattice parameter is $a_0 = 7.87$ Å and there are 8 formula units per cell[11], this is equal to 410 emu /cm^3 at 5 K, which means 2.7 μ_B per Gd ion. This is a factor of 2.6 smaller than the reported value, 7.2 μ_B [12]. This seems to originate from unsaturated domains due to pinning centers developed while grinding the brittle ingot sample.

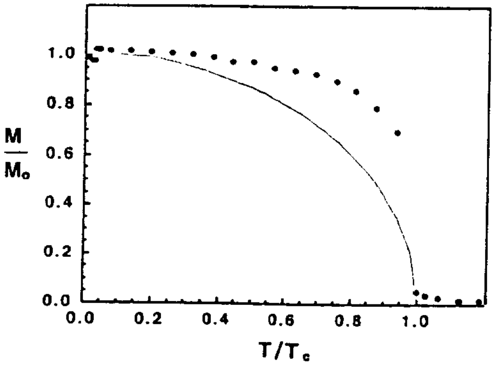

Fig. 8 The spontaneous magnetization versus temperature of $GdAl_2$ in the ferromagnetic state. The line is the theoretical curve for $J = 7/2$.

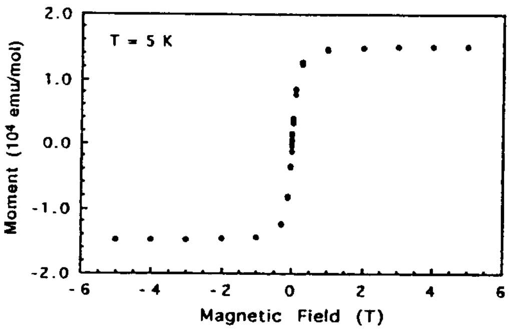

Fig. 9 The magnetization curve of $GdAl_2$ in the ferromagnetic state.

In the ferromagnetic state of $GdAl_2$, the internal field sets in due to the spontaneously ordered moments. Utilizing this internal field, we also observed ^{27}Al NMR signal around 36~43 MHz in a zero external field (Fig. 10). This means that the internal field at the aluminum sites in the ferromagnetic states is approximately 4 T [13, 14]. The zero-field ^{27}Al NMR frequency decreases at high temperatures. The temperature dependence of the zero-field ^{27}Al resonance frequency comes from the

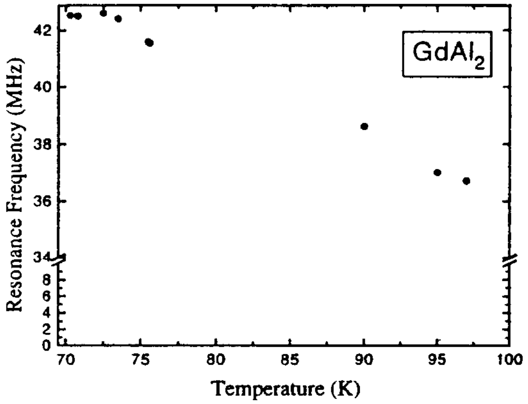

Fig. 10 The temperature dependence of zero-field ^{27}Al NMR frequency for $GdAl_2$ in the ferromagnetic state.

thermal excitation of spin wave, of which an energy quantum is so called the magnon. The average number of thermally excited magnons increases as temperature increases, which decreases the magnitude of spontaneous magnetization and consequently the internal field strength. The decrease of spontaneous magnetization is known to be proportional to $T^{3/2}$. Hence the zero-field ^{27}Al NMR frequency decreases at high temperatures, as observed in Fig. 10, since it is just proportional to the internal magnetic field at the probing nuclear site, aluminum.

In summary, $LuAl_2$ exhibits the characteristic behavior of nonmagnetic metals whereas $CeAl_2$ and $GdAl_2$ show prominent magnetism due to the 4f moments as well as conductivity due to the intervening aluminum orbitals. Both $CeAl_2$ and $GdAl_2$ undergo magnetic orderings. However, the ground states of two systems are different ; the antiferromagnetic state below 4 K for $CeAl_2$ and the ferromagnetic state below 170 K. Also the effective numbers of magnetic moments in the paramagnetic states are observed to be consistent with the orbital picture of Ce^{+3} and Gd^{+3}. As mentioned in the introduction, Ce^{+3} and Gd^{+3} ions have the partially filled 4f bands by 1 and 7 electrons, respectively. On the other hand, Lu^{+3} does not carry any local moments due to the completely filled 4f bands by 14 electrons [8]. Therefore the distinctive magnetic properties observed from RAl_2 (R ; Lu, Ce, Gd) originate from the different 4f band fillings.

Ⅳ. Conclusions

The magnetic susceptibility of $LuAl_2$ is temperature independent and shows the Pauli susceptibility. The value of spin susceptibility for $LuAl_2$ is 10.1×10^{-5} emu/mol after the core diamagnetic susceptibility correction, which means 3.2 states/eV/formula unit. On the other hand, the susceptibility data of $CeAl_2$ and $GdAl_2$ show a Curie-Weiss behavior in the paramagnetic states. The Curie constants and Curie-Weiss temperatures are respectively 0.67 emu. K/mol and −24 K for $CeAl_2$ and 3.07 emu. K/mol and 163 K for $GdAl_2$. From the Curie constants the effective numbers of moments are calculated to be 2.39 and 5.11 respectively for $CeAl_2$ and $GdAl_2$. These values are roughly consistent with the orbital pictures of Ce^{+3} and Gd^{+3}. The susceptibility data suggest that $CeAl_2$ undergoes an antiferromagnetic phase transition near 4 K whereas $GdAl_2$ does a ferromagnetic transition at 170 K. The zero field ^{27}Al NMR frequency for $GdAl_2$ indicates the internal field in the ferromagnetic state of $GdAl_2$ is roughly 4 T at the aluminum sites. The observed magnetic properties and structures of RAl_2 (R ; Lu, Ce, Gd) are distinctively different. These originate from the different 4f band filling.

This work was supported by Non-directed Research Fund, Korea Research Foundation, 1993. This work was also supported by Basic Science Research Institute Program, Ministry of Education.

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희토류원소-알루미늄 화합물 RAl$_2$의 자기적성질 및 구조

이무희 · 엄승욱 · 박태경
건국 대학교 이과대학 물리학과, 서울 133-701

(1995년 5월 25일 받음, 1995년 6월 28일 최종수정본 받음)

희토류-알루미늄 금속합금, RAl$_2$ (R ; Lu, Ce, Gd) 를 arc-melt 방법으로 제조하였으며, 이들의 자기적성질 및 전자구조를 초전도양자간섭소자를 이용한 자기감수율 측정으로 연구 하였다. LuAl$_2$의 자기감수율은 온도에 거의 무관하고 10.1×10^{-5} emu/mol 크기의 Pauli 자화율을 보였다. 이로부터 얻어진 Fermi 준위에서의 전자상태밀도는 3.2 states/eV/formula unit였다. 한편 CeAl$_2$와 GdAl$_2$의 자기감수율은 상자성체의 Curie-Weiss 법칙을 따랐다. 저온에서의 자화곡선은, CeAl$_2$의 경우 4 K에서 반강자성적 상전이를 하고 GdAl$_2$의 경우 170 K에서 강자성적 상전이를 함을 보였다. 세가지 시료의 현저히 다른 자기적성질은 4f 밴드의 채움이 각기 다름에 기인한다.