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Ferromagnetism of $(ScCa)Co_2$ Laves phase compound synthesized under high pressure

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Abstract

The appearance of ferromagnetism in $(Sc_{0.85}Ca_{0.15})Co_2$ Laves phase synthesized under high pressure of 6 GPa was confirmed. A magnetically homogeneous state was achieved by applying pressure of 6 GPa in 1373 K for 48 h. This is the first study that confirmed a stable ferromagnetic state in exchange-enhanced Pauli paramagnet $ScCo_2$-based compound system. The quantities of pressure P and magnetization M dependence of the Curie temperature T_C, $\mathrm{dln}\,T_C/\mathrm{d}P$ and $(\mathrm{dln}\,T_C/\mathrm{d}P)/(\mathrm{dln}\,M/\mathrm{d}P) = \mathrm{dln}\,T_C/\mathrm{dln}\,M$ for $(Sc_{0.85}Ca_{0.15})Co_2$ are smaller than those for $Lu(Co_{1-x}Al_x)_2$ compounds, and accordingly the magnetic moment of $(Sc_{0.85}Ca_{0.15})Co_2$ is stiffer against pressure. The ratio of the spin wave stiffness constant D_s to T_C, D_s/T_C, in $(Sc_{0.85}Ca_{0.15})Co_2$ is smaller than that of $Lu(Co_{1-x}Al_x)_2$, implying that the spin wave in $(Sc_{0.85}Ca_{0.15})Co_2$ spread over wider wavevector space.
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1. Introduction

C-15 type RCo_2 Laves phase compounds with R (rare earth and transition metal element) for IIIB group metals such as Sc, Y and Lu exhibit an exchange enhanced Pauli paramagnetism [1–4]. From the band calculations for these compounds, it has been pointed out that a sharp density of states (DOS) peak lies just below the Fermi level [5]. By applying high magnetic field, a metamagnetic transition from the paramagnetic to the ferromagnetic state occurs at 69 T for YCo_2 and 74 T for $LuCo_2$ [6,7]. Moreover, a ferromagnetic state is induced by a slight change of the electronic structure, that is, a ferromagnetic state is established by partial substitution of Co for Al or Ga in $LuCo_2$ [8,9]. A weak ferromagnetic state with a low Curie temperature $T_C \approx 20$ K also appears by partial substitution of Co for Al or Ga in YCo_2 [10]. However, no clear evidence for appearance of the ferromagnetic state in $ScCo_2$ system has been reported [11]. It has been pointed out that the partial substitution of Al in YCo_2 leads to smoothing of the sharp peak of the DOS [12], fading the characteristics of band magnetism.

The shift of Fermi level with respect to the substitution of the R element in RCo_2 has been theoretically discussed [5,13]. When the R-site is replaced by Ti, the d-electron number increases and the Fermi level E_F shifts toward a higher energy side far from main peak of DOS, resulting in a paramagnetic $TiCo_2$ [13]. On the other hand, E_F shifts to lower energy side by replacing R by Ca, and E_F is located at just on the main peak of DOS [13], stabilizing the ferromagnetic state in $CaCo_2$ [14]. For the systems substituted the R-site in $CaCo_2$, $ScCo_2$ and $TiCo_2$, a rigid band like concept is valid. In order to confirm the band magnetism expected in the theoretical discussion, the partial substitution of Sc for Ca in $ScCo_2$ has been examined in the present study. Since the existence of C-15 type $(ScCa)Co_2$ has not been confirmed yet, we have synthesized $(ScCa)Co_2$ by applying high-pressure of 6 GPa. The magnetic properties are compared with those of $Lu(Co_{1-x}Al_x)_2$ Laves phase compounds.

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2. Experimental

Before synthesizing $(ScCa)Co_2$, $ScCo_2$ was prepared by arc melting in an Ar gas atmosphere and $CaCo_2$ was prepared by a high-pressure synthesis method under 6 GPa in 1173 K for 2 h. Both compounds $ScCo_2$ and $CaCo_2$ were crashed into powders with about 100 μm. These powders were mixed in the ratio of 85:15. $(Sc_{0.85}Ca_{0.15})Co_2$ was synthesized under 6 GPa in 1373 K for several different times. The crystal structure was identified by X-ray powder diffraction using Kα spectrum of Cu with wavelength $\lambda = 1.5416$ nm. The magnetization measurement was carried out with a SQUID magnetometer. The pressure up to 0.9 GPa was applied to the specimen by using a Cu-3 wt.% Ti alloy nonmagnetic pressure clamp cell. The Daphne oil 7373 was used as the transmit medium of pressure. The applied hydrostatic external pressure at low-temperature were calibrated by measuring the shift of the superconducting transition temperature of Pb.

3. Results and discussion

The X-ray diffraction patterns of $(Sc_{0.85}Ca_{0.15})Co_2$ synthesized by several different conditions are shown in Fig. 1. The diffraction peaks with underlines indices come from a C-15 type $CaCo_2$ structure with the lattice constant of 7.45 Å for the specimen synthesized in 1173 K for 2 h. The peaks become sharp with increasing synthesis temperature and time, proving the proceed of homogenization. The magnetization curves at 4.2 K for $(Sc_{0.85}Ca_{0.15})Co_2$ synthesized in 1373 K for three different times are shown in Fig. 2. With increasing synthesizing time, the magnetization increases. As seen in the figure, the saturation magnetic field is about 0.5 T and the high magnetic field susceptibility is relatively small. The magnetic moment M per Co-atom is calculated to be about 0.4 μ_B. The Arrott plots in the vicinity of the Curie temperature T_C for $(Sc_{0.85}Ca_{0.15})Co_2$ with synthesizing time of 96 h are shown in Fig. 3. Straight lines are obtained at each temperature, supporting an excellent magnetic homogeneity in the specimen and the Curie temperature T_C is decided to be 206 K. It should be pointed out that $ScCo_2$ is paramagnetic and T_C of ferromagnetic $CaCo_2$ is about 530 K [14]. Accordingly, a markedly different magnetic state is observed by a small amount substitution of Ca in $ScCo_2$. Note that similar straight lines of the Arrott plots are also obtained for the specimen synthesized in 1373 K for 48 h.

For ferromagnets with the second-order magnetic transition, T_C is one of the measures of stability of the ferromagnetic state. To discuss more clearly the stability of band ferromagnetism in $(Sc_{0.85}Ca_{0.15})Co_2$, the magnetization M measurements under hydrostatic pressure have been carried out. The thermomagnetization curves up to 0.9 GPa for $(Sc_{0.85}Ca_{0.15})Co_2$ synthesized at 1373 K for 96 h are shown in Fig. 4. Both T_C and M decrease with increasing pressure. The pressure dependence of T_C and M at 4.2 K is given in Fig. 5. From the slopes, $\mathrm{d}T_C/\mathrm{d}P$ and $\mathrm{d}M/\mathrm{d}P$ are decided to be −16 K/GPa and −0.03 μ_B/GPa, respectively. The values of T_C, $\mathrm{dln}\,T_C/\mathrm{d}P$, $\mathrm{dln}\,M/\mathrm{d}P$ at 4.2 K and $(\mathrm{dln}\,T_C/\mathrm{d}P)/(\mathrm{dln}\,M/\mathrm{d}P) = \mathrm{dln}\,T_C/\mathrm{dln}\,M$ of $(Sc_{0.85}Ca_{0.15})Co_2$ are given in Table 1, together with those of $Lu(Co_{0.85}Al_{0.15})_2$ and $Lu(Co_{0.80}Al_{0.20})_2$ Laves compounds which show the second-order magnetic phase transition from

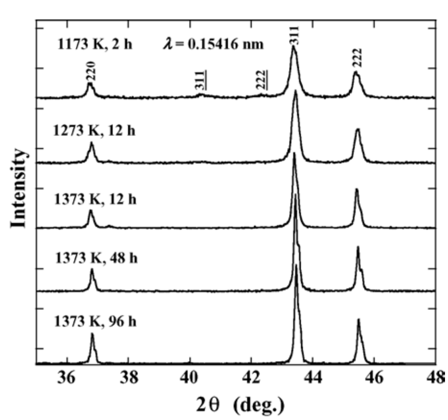

Fig. 1. Powder X-ray diffraction patterns of $(Sc_{0.85}Ca_{0.15})Co_2$ Laves phase compound synthesized applying 6 GPa under different conditions. The wavelength of X-ray is $\lambda = 0.15416$ nm.

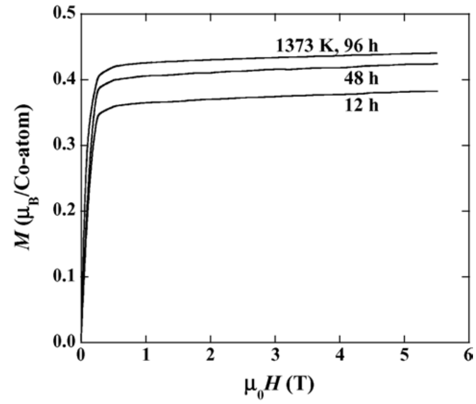

Fig. 2. Magnetization curves at 4.2 K for $(Sc_{0.85}Ca_{0.15})Co_2$ synthesized under applying pressure of 6 GPa in 1373 K for three different times.

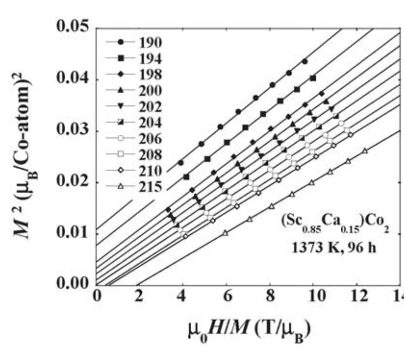

Fig. 3. Arrott plots in the vicinity of the Curie temperature $T_C = 206$ K for $(Sc_{0.85}Ca_{0.15})Co_2$ synthesized under 6 GPa in 1373 K for 96 h.

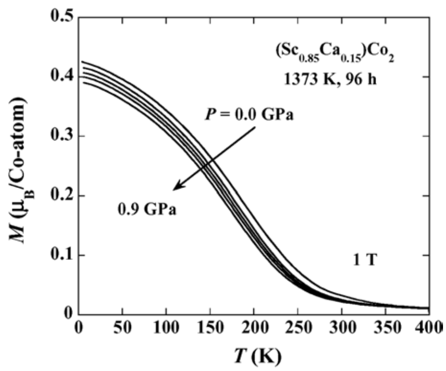

Fig. 4. Thermomagnetization curves measured by applying pressure up to 0.9 GPa for $(Sc_{0.85}Ca_{0.15})Co_2$ synthesized under 6 GPa in 1373 K for 96 h.

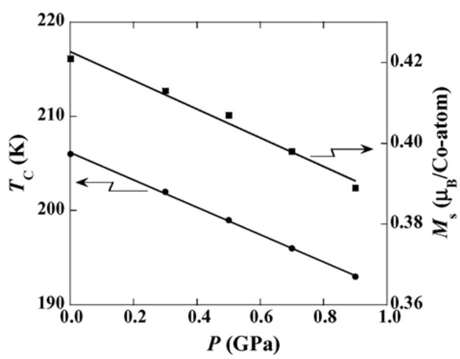

Fig. 5. Pressure dependence of the Curie temperature T_C and the magnetic moment M at 4.2 K for $(Sc_{0.85}Ca_{0.15})Co_2$ synthesized under 6 GPa in 1373 K for 96 h. dT_C/dP is −16 K/GPa and dM/dP is −0.03 μ_B/GPa.

the ferromagnetic to the paramagnetic state [9]. In addition, the compounds with $x = 0.15$–0.16 exhibit the highest T_C 130–150 K in $Lu(Co_{1-x}Al_x)_2$ system [9,15]. It should be pointed out that the present compound exhibits the highest T_C among the $ScCo_2$, YCo_2 and $LuCo_2$ based quasi-binary compound systems. The values of dM/dP for $(Sc_{0.85}Ca_{0.15})Co_2$ is the same in magnitude as that for $Lu(Co_{0.85}Al_{0.15})_2$, implying that the stiffness of the amplitude of local magnetic moment $\langle M_{loc}^2 \rangle$ against external pressure in the ground state is comparable. On the other hand, the value of $d\ln T_C/dP$ of $(Sc_{0.85}Ca_{0.15})Co_2$ is smaller than those of $Lu(Co_{1-x}Al_x)_2$ Laves phase compounds, namely, the ratio of $d\ln T_C/d\ln M$ is small. It has been reported that the thermal variation of $\langle M_{loc}^2 \rangle$ due to thermal spin fluctuations, which is significant in $Lu(Co_{1-x}Al_x)_2$ [9]. In the system, which exhibits a significant increase of thermal spin fluctuations, T_C decreases drastically on applying pressure [16], because T_C is strongly related with the renormalization effect of spin fluctuations in the magnetic free energy in the finite temperatures [16]. It has been pointed out that the positive curvature of the DOS at the Fermi level E_F remains up to around $x = 0.15$ in $Lu(Co_{1-x}Al_x)_2$, and hence a negative mode–mode coupling among spin fluctuations leads to large values of $d\ln T_C/dP$ and $d\ln T_C/d\ln M$ [9,16]. Therefore, it is expected that the difference between the shape of DOS around E_F brings about the difference in the stiffness of $\langle M_{loc}^2 \rangle$ against pressure in $(Sc_{0.85}Ca_{0.15})Co_2$ and in $Lu(Co_{0.85}Al_{0.15})_2$.

The thermal variation characteristics of local magnetic moment appears in the spin wave dispersion relation. In the itinerant-electron systems, the spin wave excitation occurs as well as the localized magnetic moment systems. In the spin wave dispersion theory, the relation between the spin wave energy ω_q and the wavevector q is given by $\hbar\omega_q = D_s q$. The spin wave stiffness constant D_s is obtained from M versus $T^{3/2}$ at low temperatures. The values of D_s and D_s/T_C for $(Sc_{0.85}Ca_{0.15})Co_2$ are given in Table 1, together with those for $Lu(Co_{1-x}Al_x)_2$ compounds. The quantity of D_s closely relates with the feature of the imaginary part of dynamical susceptibility Im $\chi(q,\omega)$. Here, the integration of Im $\chi(q,\omega)$ characterizes the thermal properties spin fluctuations [17]. In the weak itinerant-electron systems, Im $\chi(q,\omega)$ shows a strong q dependence, that is, in a small q region it extends up to high ω [17]. On the contrary, Im $\chi(q,\omega)$ exhibits a weak q dependence in localized magnetic moment systems [17]. Therefore, the ratio of D_s/T_C is the implicit measure of the spread of spin fluctuations in the q space. A small value of D_s/T_C implicates a wide spread of spin fluctuations in the q space. Note that the ratio of D_s/T_C in a weak itinerant-electron ferromagnet Ni_3Al is very large, close to 2 meV Å^2 K^{-1} [18]. The ratio of D_s/T_C for $(Sc_{0.85}Ca_{0.15})Co_2$ is about 0.4 and it is much smaller than that of the isostructure $Lu(Co_{1-x}Al_x)_2$. Comparing the ratio of D_s/T_C, it is considered that the excitations of spin wave spread wider in the q space in $(Sc_{0.85}Ca_{0.15})Co_2$ than in $Lu(Co_{1-x}Al_x)_2$ system. In both systems, the ferromagnetic state appears by a partial substitution in exchange-enhanced Pauli paramagnets. However, the mechanism of the onset of ferromagnetism in the former R-site substitution system is different from the latter Co-site substituted system. It has been pointed out that the smoothing of DOS peaks occurs due to alloying effect of Co-band when Co is partially substituted by Al in YCo_2 and a slight increase of DOS at the Fermi level E_F brings about appearance of ferromagnetism [12]. In $Lu(Co_{1-x}Al_x)_2$ systems, the onset of ferromagnetism

Table 1
The Curie temperature T_C, quantities of pressure effect $d\ln T_C/dP$, $d\ln M/dP$ at 4.2 K and $d\ln T_C/d\ln M$, spin wave stiffness constant D_s and the ratio of D_s/T_C for $(Sc_{0.85}Ca_{0.15})Co_2$, $Lu(Co_{0.85}Al_{0.15})_2$ and $Lu(Co_{0.80}Al_{0.20})_2$ Laves compounds

	T_C (K)	$d\ln T_C/dP$ (GPa^{-1})	$d\ln M/dP$ (GPa^{-1})	$d\ln T_C/d\ln M$	D_s (meV Å^2)	D_s/T_C (meV Å^2 K^{-1})
$(Sc_{0.85}Ca_{0.15})Co_2$	206	−0.08	−0.08	1.0	81	0.39
$Lu(Co_{0.85}Al_{0.15})_2$	131	−0.23	−0.07	3.2	146	1.11
$Lu(Co_{0.80}Al_{0.20})_2$	103	−0.17	−0.15	1.1	106	1.03

should be similar to $Y(Co_{1-x}Al_x)_2$, although the critical Al concentration for the onset of ferromagnetism in the former is lower than that in the latter [9]. On the other hand, the substitution of Ca for Sc in $ScCo_2$, the position of E_F shifts towards the main peak [13]. It can be considered that the characteristic band shape for RCo_2 Laves phase, that is, the sharp main peak near E_F, still remains after substitution of Sc for Ca in $ScCo_2$, leading to stable ferromagnetic state. As a consequence, the renormalization effect of thermal spin fluctuations is weaker than that of Co-site substituted systems mentioned above.

4. Conclusion

The appearance of ferromagnetic state in $(Sc_{0.85}Ca_{0.15})Co_2$ Laves phase compound synthesized under high pressure has been investigated. Experimentally, the stable ferromagnetic state has been confirmed for the first time in $ScCo_2$-based compound system. The ferromagnetic properties, the Curie temperature T_C and the magnetization M, have been investigated. The main results are summarized as given further.

(1) For the synthesis of $(Sc_{0.85}Ca_{0.15})Co_2$, application of pressure 6 GPa in 1373 K for 48 h gives a magnetically well homogenized phase.
(2) The quantities of pressure effects such as $\mathrm{d}\ln T_C/\mathrm{d}P$ and $\mathrm{d}\ln T_C/\mathrm{d}\ln M$ in $(Sc_{0.85}Ca_{0.15})Co_2$ are smaller than those of $Lu(Co_{1-x}Al_x)_2$ compounds, suggesting the difference between the shape of DOS around E_F.
(3) The ratio of the spin wave stiffness constant D_s to T_C, D_s/T_C, in $(Sc_{0.85}Ca_{0.15})Co_2$, is much smaller than that in $Lu(Co_{1-x}Al_x)_2$ and weak ferromagnetic systems, implying that the spin wave spread wide in the q space.

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