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Ferromagnetic enhancement in the hexagonal $Ce(Rh_{1-x}Ir_x)_3B_2$ system

S. W. Hsu and H. C. Ku

Department of Physics, National Tsing Hua University, Hsinchu, Taiwan 30043, Republic of China

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Electrical resistivity, magnetization, and crystallographic measurements have been carried out for the pseudoternary system $Ce(Rh_{1-x}Ir_x)_3B_2$. A single-phase hexagonal $CeCo_3B_2$-type structure persists from $x=0.0$ up to $x<0.75$, through a narrow two-phase region at higher iridium concentration, and transforms to a monoclinic $ErIr_3B_2$-type structure for $x>0.95$. The ferromagnetic Curie temperature T_C is enhanced from 115 K for $CeRh_3B_2$ to 125 K for $Ce(Rh_{0.8}Ir_{0.2})_3B_2$, then decreases slowly to 118 K at $x=0.5$ before decreasing sharply to 69 K at $x=0.67$, even though the magnetic moment per Ce ion decreases monotonically with increasing Ir substitution. The T_C of 125 K in $Ce(Rh_{0.8}Ir_{0.2})_3B_2$ is the highest magnetic-ordering temperature observed so far for all Ce-based systems with nonmagnetic constituents.

Recently, the ternary cerium boride $CeRh_3B_2$ has received much attention due to its unusual magnetic properties. The Ce ions of $CeRh_3B_2$ form chains along the hexagonal c axis with a very short intrachain Ce-Ce distance of only 3.09 Å.[1,2] An anomalous high ferromagnetic transition with the Ce moments ordering along the c axis below $T_C=115$ K has been reported.[3-21] Even for such high T_C, the saturation moment at low temperature is only 0.3–$0.4\mu_B$ per Ce ion, which is much smaller than the Ce^{3+} free-ion moment of $2.14\mu_B$.[7] Because of large $4f$-$4f$ direct mixing, the $4f$ state has strong dispersion along the c direction, and is the origin of the anomalous magnetic properties.[22-24]

Above T_C, the $4f$ paramagnetic ground state is $J_z=\pm\frac{1}{2}$ and the excited states are thought to be at fairly high energies. At higher temperature, all the crystal-field states are nearly equally populated and then the system behaves like a dense Kondo system.[24] Bremsstrahlung isochromat spectroscopy (BIS) spectra and valence-band Ce $3d$ x-ray photoemission spectroscopy (XPS) spectra are consistent with $n_f \cong 1$, but show hybridization more typical of high Kondo temperature T_K materials with $n_f<1$. Proof of the Kondo state was obtained from studies of the pseudoternary compound $Ce(Rh_{1-x}Co_x)_3B_2$, where the resistivity increases with decreasing temperature during the initial cool-down and a local minimum Kondo anomaly was observed around 210 K.[17]

The substitution of Ru, Os, or Co for Rh leads to rapid depression of both the Curie temperature and the saturation moment.[11-14,17,19] Although Ir and Rh are in the same column of the Periodic Table, the compound $CeIr_3B_2$ crystallizes in a monoclinic $ErIr_3B_2$-type structure which is closely related to the hexagonal $CeCo_3B_2$-type structure and is a nonmagnetic, intermediate valence compound.[25-27] In this report, we study the pseudoternary system $Ce(Rh_{1-x}Ir_x)_3B_2$ and find out that with 20% substitution of Rh by Ir, T_C can be enhanced from 115 K for $CeRh_3B_2$ to 125 K.

All samples were prepared by arc melting the high-purity elements (Ce, Rh, Ir: 99.9%, B: 99.9995%) under an ultrahigh-purity (UHP) argon atmosphere in a Zr-gettered arc furnace. The arc-melted samples were carefully annealed at 1000 °C for one week by wrapping in Ta foil and then sealed under argon in a quartz tube, followed by quenching to room temperature in water. Powder x-ray-diffraction data were obtained through a Shimadzu XD-3 diffractometer with CuK_α radiation.

Magnetization and magnetic-susceptibility measurements were obtained on powder samples using a PAR-155 vibrating sample magnetometer (VSM) with an applied magnetic field of 1 T and temperature range from 5 to 300 K. Low-frequency (16-Hz) ac electrical resistivity measurements were made between 10 and 300 K in a Cryosystems LTS-21 closed cycle refrigerator using standard four-probe method. The electrical leads (76.2-μm Pt wire) were spot welded to the samples.

Temperature dependence of the electrical resistivity of $Ce(Rh_{0.8}Ir_{0.2})_3B_2$ for both cool down (no temperature control with average cooling rate of 8 K/min) and warm up (with temperature control) are shown in Fig. 1, along with magnetic moment per Ce ion in an applied field of 1 T. The resistivity of the sample in the initial cool down decreases slowly with decreasing temperature down to 125 K, where a sharp decrease in the resistivity is well corre-

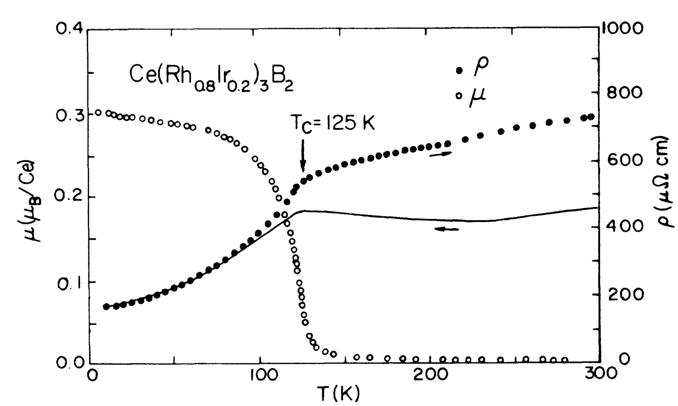

FIG. 1. Electrical resistivity $\rho(T)$ and magnetic moment per Ce ion $\mu(T)$ (in an applied field of 1 T) of pseudoternary compound $Ce(Rh_{0.8}Ir_{0.2})_3B_2$ with Curie temperature $T_C=125$ K. The local minimum of resistivity at 210 K can be easily seen in the cool-down curve.

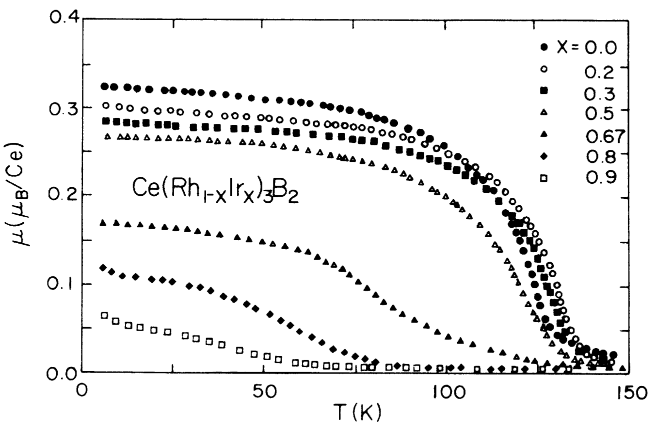

FIG. 2. Temperature dependence of magnetization (in magnetic moment per Ce ion) of $Ce(Rh_{1-x}Ir_x)_3B_2$ powder samples in an applied field of 1 T.

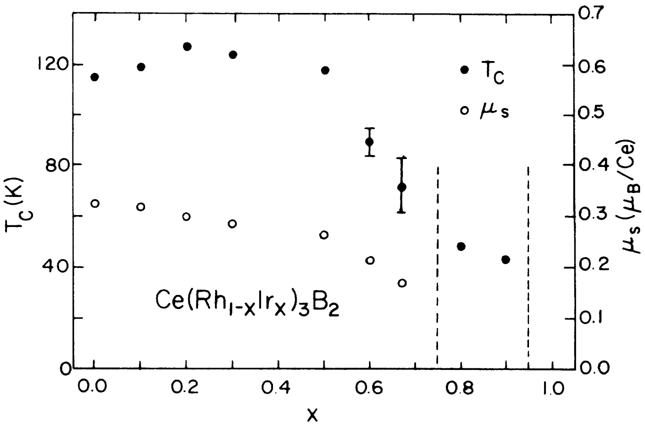

FIG. 3. Composition variation of Curie temperature T_C and saturation magnetic moment per Ce ion of the pseudoternary system $Ce(Rh_{1-x}Ir_x)_3B_2$. A two-phase region appears between $x = 0.75$ and $x = 0.95$.

lated with the ferromagnetic ordering temperature obtained from magnetization measurement. A T_C of 125 K is 10 K higher than 115 K for $CeRh_3B_2$ and is the highest value observed so far for Ce systems with nonmagnetic constituents. The resistivity value at room temperature is 460 $\mu\Omega$ cm in the initial cool-down, and down to a residual value $\rho_0 = 172$ $\mu\Omega$ cm at 10 K, which gives a resistivity ratio of 2.7. In the warm-up process from 10 K, the resistivity follows the cool-down curve exactly up to near the Curie temperature, and then increases more rapidly with increasing temperature, giving a new room-temperature value of 730 $\mu\Omega$ cm and a resistivity ratio of 4.2. This extra contribution of electrical resistivity is believed to be originated from the occurrence of microscopic cracks during warm-up process. Since the resistivity irreversibility occurs near Curie temperature T_C, it is possible that these microscopic cracks may be created by ferromagnetic-transition-related stress and the extreme brittleness of these ternary cerium borides.[17] The paramagnetic resistivity above T_C in the initial cool-down shows evidence of Kondo-type local minimum anomaly around 210 K which was also observed in the isostructural system $Ce(Rh_{1-x}Co_x)_3B_2$.[17,19] Using the equation $\rho = \rho_0 + AT^n$ to the resistivity below T_C, the exponent n is found close to 2 perfectly and can be interpreted as the presence of strong interband scattering between conduction electrons and the band of collective states.

Temperature dependence of magnetization in a 1-T applied field in terms of magnetic moment per Ce ion for powder samples of the $Ce(Rh_{1-x}Ir_x)_3B_2$ system are shown in Fig. 2. The saturation magnetic moment decreases monotonically with increasing Ir substitution. However, an interesting crossover of the magnetization curves near ferromagnetic ordering temperature in the lower Ir concentration region clearly indicates the enhancement of T_C, which is also observed in electrical resistivity measurements. The composition variation of T_C from both resistivity and magnetization measurements, and the saturation moment μ_s of these pseudoternary compounds are shown in Fig. 3 and listed in Table I, along with the paramagnetic effective moment per Ce ion (μ_{eff}), Curie-Weiss paramagnetic intercept (θ_p), and temperature-independent susceptibility (χ_0). The T_C in-

TABLE I. Hexagonal lattice parameters (a and c), unit-cell volume (V), Curie temperature (T_C), saturation magnetic moment per Ce ion (μ_s), effective moment (μ_{eff}), Curie-Weiss paramagnetic intercept (θ_p), and the temperature-independent susceptibility (χ_0) in the $Ce(Rh_{1-x}Ir_x)_3B_2$ system.

x	a (Å) ($\pm$0.005)	c (Å) ($\pm$0.003)	V (Å^3) ($\pm$0.08)	T_C (K)	μ_s (μ_B/Ce)[a]	μ_{eff} (μ_B/Ce)	θ_p (K)	χ_0 (cm^3/mol)
0.0	5.469	3.090	80.04	115(1)	0.324	1.01	120	5.57
0.1	5.470	3.088	80.02	118(1)	0.318	0.946	123	0.943
0.2	5.473	3.088	80.10	125(1)	0.301	0.898	129	0.815
0.3	5.472	3.090	80.13	123(1)	0.283	0.859	126	. . .
0.5	5.475	3.088	80.17	118(2)	0.266	0.932	121	0.681
0.6	5.476	3.092	80.30	90(5)	0.215	0.863	100	. . .
0.67	5.489	3.092	80.68	69(11)	0.170	. . .	. . .	. . .
0.8[b]	5.500	3.094	81.05	47	. . .	. . .	. . .	. . .
0.9[b]	. . .	. . .	. . .	43	. . .	. . .	. . .	. . .

[a] 1-T applied magnetic field.

[b] Two-phase compounds.

creases from 115 K for $CeRh_3B_2$ to 118 K at $x=0.1$ and reaches the record high value of 125 K for $Ce(Rh_{0.8}Ir_{0.2})_3B_2$ then decreases slowly to 118 K at $x=0.5$ before dropping sharply to 69 K at $x=0.67$ and 47 K at $x=0.8$. $Ce(Rh_{0.2}Ir_{0.8})_3B_2$ ($x=0.8$) is a two-phase compound with approximately 70% of $CeCo_3B_2$-type phase while a single-phase boundary occurs around $x\simeq0.75$. No magnetic ordering was observed for monoclinic $ErIr_3B_2$-type single-phase compounds ($x>0.95$).

Variation of paramagnetic Curie-Weiss intercept θ_p (Table I) from the magnetic susceptibility χ measurements above T_C using the formula $\chi=\chi_0+C/(T-\theta_p)$, where χ_0 is the temperature-independent component of magnetic susceptibility and C is the Curie constant, is consistent with the variation of T_C with the maximum value θ_p of 129 K at $x=0.2$. The effective moments derived from Curie constant C are still smaller than the Ce^{3+} effective moment of $2.54\mu_B$; this indicates the intermediate-valence nature of these cerium compounds in the paramagnetic state.

Hexagonal lattice parameters a, c and unit-cell volume V of the $Ce(Rh_{1-x}Ir_x)_3B_2$ system as a function of the Ir parameter x are shown in Fig. 4 and listed in Table I. For $x\leq0.5$, the hexagonal c parameter (equal to the Ce-Ce distance) keeps almost the same value of 3.09 Å, while the unit-cell volume V increases slowly from 80.04(8) Å^3 for $CeRh_3B_2$ to 80.17(8) Å^3 for $Ce(Rh_{0.5}Ir_{0.5})_3B_2$ before sharply increasing to 80.30(8) Å^3 for $Ce(Rh_{0.4}Ir_{0.6})_3B_2$ and 80.68(8) Å^3 for $Ce(Rh_{0.33}Rh_{0.67})_3B_2$. These data suggest that when the Rh atoms are progressively substituted by larger Ir atoms, the variation of ferromagnetic Curie temperature T_C is well correlated with the variation of unit-cell volume. The hexagonal $CeCo_3B_2$-type single phase ends around $x=0.75$, follows with a two-phase region for $0.75\leq x\leq0.95$, and then transforms into a single-phase monoclinic $ErIr_3B_2$-type region for $x>0.95$.

The magnetic properties of these compounds are determined by both short Ce-Ce direct mixing and strong interaction of the localized Ce ions with the conduction electrons which is dominated by Rh and Ir bands. In the Rh-rich region, with anomalous small change of the unit-cell volume, the electron density of states at the Fermi level E_F is expected to increase due to more extended Ir $5d$ bands. This increasing electron density of states at E_F will enhance the hybridization between the conduction electrons and Ce ions which makes the $4f$ electron of Ce ions more delocalized with resulting smaller saturation magnetic moment and pronounced Kondo behavior. Also, the indirect Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction among Ce magnetic moments will increase its strength through the increasing conduction electron density and is believed to be the key factor for the enhanced ferromagnetic transition temperature in the present system. For Ir replacement higher than $x=0.6$, the hexagonal lattice parameters a, c and unit-cell volume V increase rapidly along with the suppression of both Curie temperature and saturation magnetic moment.

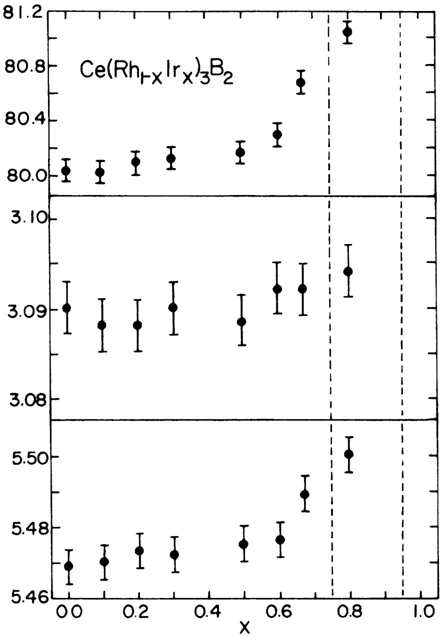

FIG. 4. Hexagonal lattice parameters (a and c) and unit-cell volume V in the $Ce(Rh_{1-x}Ir_x)_3B_2$ system. A two-phase region appears between $x=0.75$ and $x=0.95$.

In conclusion, the anomalous high Curie temperature T_C of 125 K was observed in the pesudoternary compound $Ce(Rh_{0.8}Ir_{0.2})_3B_2$. This transition temperature is the highest magnetic ordering temperature observed so far for all Ce-based systems with nonmagnetic constituents.

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