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Magnetic properties and resistivity of ternary compounds $CeNi_2X_2$ (X=Sb, As, P)

H. Suzuki[a,b,]*, H. Abe[a], H. Kitazawa[a], D. Schmitt[b]

[a]*National Research Institute for Metals, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan*
[b]*Laboratoire Magnetisme Louis Néel, CNRS, 25 Avenue des Martyrs, BP 166, 38042 Cédex 9, France*

Abstract

The series of the ternary pnictides $CeNi_2X_2$ (X=Sb, As and P) for both $CaBe_2Ge_2$-type and $ThCr_2Si_2$-type structures have been investigated by the measurements of the magnetic susceptibility and the electrical resistivity. In the $CaBe_2Ge_2$-type structure, the characteristic energy scale of the Kondo effect increases with the decrease of the volume from X=Sb to As. The ground state for X=As is non-magnetic due to the Kondo effect. In the $ThCr_2Si_2$-type structure, the systems show a drastic change from the Kondo lattice with the magnetic ordering for X=As to the intermediate valence for X=P with the decrease of the volume only by 8%.

Keywords: Intermetallics; Crystal field; Kondo effect

A large number of ternary intermetallic phases of Rare-earth (R), transition metals (T) and normal metals or metalloids (X) have the formula RT_2X_2 and crystallize with the tetragonal structure $ThCr_2Si_2$-type (space group *I4/mmm*) or $CaBe_2Ge_2$-type (space group *P4/nmm*). While numerous studies have been devoted for X=Si and Ge compounds [1], there are few reports on the magnetic properties for the ternary pnictides systems (X=Sb, As and P) because of the difficulty in preparation. On the other hand, the CeT_2X_2 family has been widely studied from the viewpoint of the Kondo lattice system. Possible combinations of the elements of T and X introduce the variety of the relation of the energy scales among the Kondo effect, the inter-site magnetic interaction and the crystal field (CF), showing the divers and/or unusual properties.

We have investigated the series with Ni as T and pnictogens as X, $CeNi_2X_2$ (X=Sb, As, P) and reported here the magnetic and transport properties. X=Sb and As of $CeNi_2X_2$ crystallize in the $CaBe_2Ge_2$-type structure, and X=As and P in the $ThCr_2Si_2$-type one, i.e. both crystal structures are realized for X=As [2,3]. $ThCr_2Si_2$-type and $CaBe_2Ge_2$-type consist in stackings of R, T and X layers with the sequence T-X-R-X-T and T-X-T-R-X-T-X-R-T, respectively, giving the different environment of the Ce ion from each other. The ratio of the tetragonal lattice parameter, a/c, is also changed between these two structures, while the unit cell volume increases almost linearly with the ionic radii of X (see Fig. 1).

The samples of $CeNi_2X_2$ were obtained through some processes as follows [4]. For X=As and P, the powder of the Ce–Ni alloy and X shots were pre-reacted in an evacuated quartz tube and, subsequently, they were sealed in W crucibles in a high vacuum. For X=Sb, the Ce–Ni alloys and Sb shots were sealed in Mo crucible directly. The only obtained single crystals of $CaBe_2Ge_2$-type $CeNi_2X_2$ (X=Sb and As) measure about 10–30 mg. For X=As, it was found that the occurrence of the $CaBe_2Ge_2$-type and $ThCr_2Si_2$-type structures depends on both the heat treatment and the composition of the element in the pre-reaction [2,3]. For X=P, the obtained sample was porous and fragile. The magnetic susceptibility, $\chi(T)$, was measured using a SQUID magnetometer. The electrical resistivity, $\rho(T)$, was measured by a conventional d.c. 4-probe method.

Fig. 2 (a) shows $\chi(T)$ for $CaBe_2Ge_2$-type on the logarithmic T-scale. For both X=Sb and As, $\chi(T)$ at low temperatures exhibit rather small but the similar anisotropic behavior as is seen in the $CaBe_2Ge_2$-type Ce-

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*Corresponding author. Tel.: +33-4-7688-7915; Fax:+33-4-7688-1191.

E-mail address: suzuki@labs.polycnrs-gre.fr (H. Suzuki).

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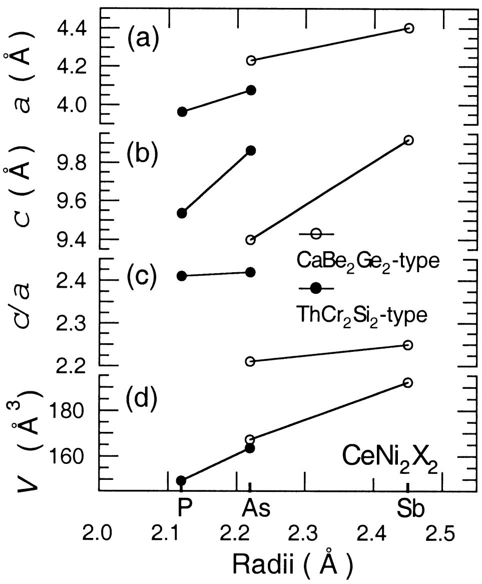

Fig. 1. The lattice parameters of the tetragonal (a) a- and (b) c-axes, (c) the ratios of a/c and (d) the volume of the unit cell as a function of the standard radii for ions.

compounds [5–7]. For X=As, the T-slope of $\chi_{\perp}$($H \perp c$-axis) becomes smaller below about 15 K, whereas $\chi_{//}(T)$($H//c$-axis) does not show the corresponding anomaly. The change in the T-slope of $\chi_{\perp}(T)$ below 15 K is considered to connect with the Kondo effect. This will be discussed later. Around 15 K, i.e. above the temperatures of the anomalous $\chi_{\perp}(T)$, the ratio of $\chi_{\perp}$ to $\chi_{//}$ of X=As is a little larger than that of X=Sb. At higher temperatures above 100 K, $\chi_{\perp}(T)$ can be described by a Curie–Weiss (CW) law with an effective moment μ_{eff}=2.33 and 2.40 μ_{B}, and the CW temperature $\Theta_{\mathrm{P}}=-6.7$ and -35.9 K for X=Sb and As, respectively. The obtained μ_{eff} is slightly smaller than that expected for the free Ce^{3+} (2.54μ_{B}) ion. For X=Sb, $\Theta_{\mathrm{P},\perp}$ is much smaller than those of polycrystalline in Refs. [8,9], but comparable to $\Theta_{\mathrm{P},\perp}$ of CePt$_2$Sn$_2$ and CeNi$_2$Sn$_2$ [6,7]. On the other hand, the T-dependence of $\chi_{//}$ becomes smaller with the increase of the temperature, resulting in that $\chi_{//}(T)$ can not be fitted by the CW law. This is probably because the contribution of the T-independent Pauli paramagnetism to χ is also anisotropic and its component for $H//c$-axis is too large to be neglected for the estimation of the magnetic contribution to $\chi_{//}(T)$ at higher temperatures.

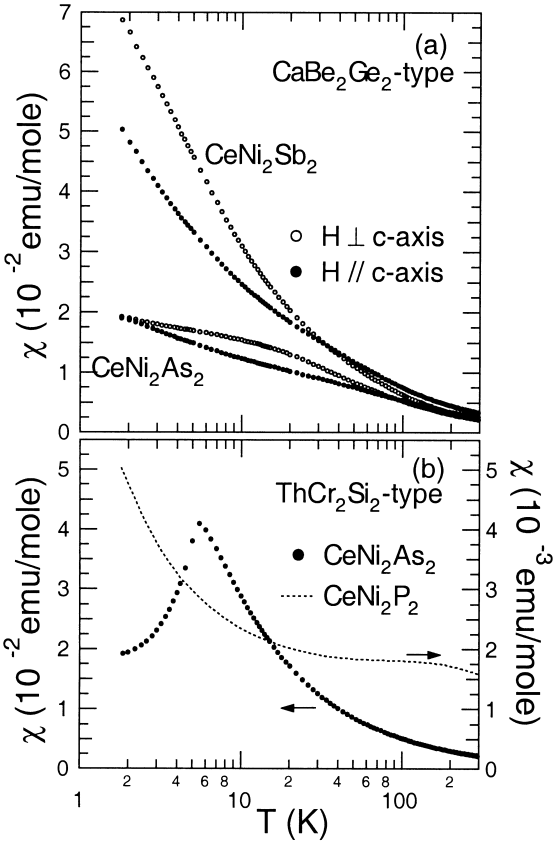

Fig. 2. The temperature dependence of the magnetic susceptibility for (a) CaBe$_2$Ge$_2$-type structure and (b) ThCr$_2$Si$_2$-type structure.

For the polycrystalline samples of ThCr$_2$Si$_2$-type, $\chi(T)$ is plotted in Fig. 2 (b). For X=As, $\chi(T)$ shows a sharp peak at 5.5 K corresponding to the antiferromagnetic ordering [2]. At higher temperatures, the CW behavior is reasonably well followed. From the fitting of $1/\chi(T)$ above 100 K, the corresponding values of μ_{eff} and Θ_{P} are obtained as 2.46 μ_{B} and 50.0 K, respectively. For X=P, the T-dependence of χ is quite weak, except for the low-T part, and does not correspond to the expectations for a Ce^{3+} ion, indicating that this compound belongs to the intermediate valence system [10]. The low-T sharp upturn could be due to impurities.

Fig. 3 shows $\rho(T)$ for all the samples measured. For the single crystals of CaBe$_2$Ge$_2$-type, $\rho(T)$ was measured only for $j \perp c$-axis. For X=Sb, $\rho(T)$ is almost T-independent around 50 K and increases up to a value larger than $\rho(T=300$ K) with the decrease of the temperature below 20 K. As shown in the inset of Fig. 3, $\rho(T)$ show a peak about 2.3 K, where $\chi(T)$ shows no anomaly. It was reported that the peak corresponding to the antiferromagnetic ordering was observed near 1 K in the specific heat measurement [9]. Then, the peak in $\rho(T)$ is the Kondo coherence peak. For the Kondo system in the presence of the CF, the temperature of the coherence peak is thought to be connected with the characteristic energy scale of the Kondo effect for the CF ground state, $T_{\mathrm{K}}^{\mathrm{eff}}$. On the other hand, the plateau of $\rho(T)$ around 50 K indicates a broaden peak or shoulder-like T-dependence of the magnetic contribution to $\rho(T)$, which originates from the reduction of the Kondo scattering due to the CF splitting. The temperature of this anomaly is roughly proportional to the energy scale of the CF splitting [11,12]. For X=As of CaBe$_2$Ge$_2$-type, $\rho(T)$ is characterized by the two shoulders about 15 and 100 K. It is noted that the temperature of the lower-T shoulder is consistent with that of the cross over into the T-independent behavior in $\chi_{\perp}(T)$. Moreover, down to 1.5

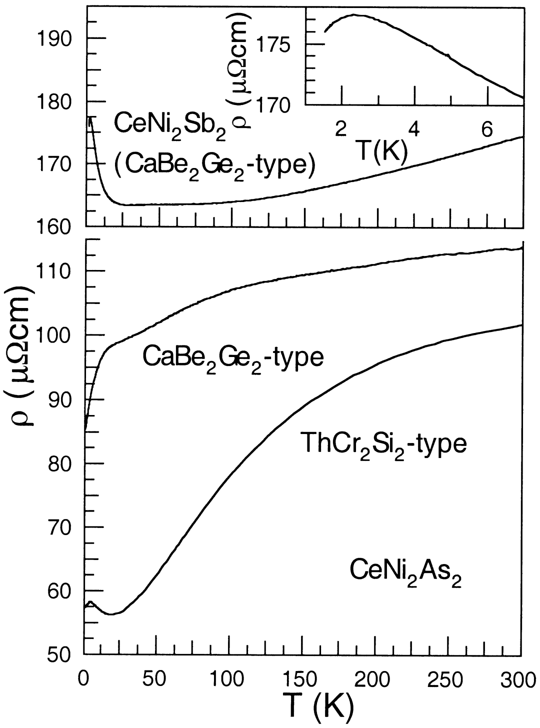

Fig. 3. The temperature dependence of the resistivity. The low temperature part for X=Sb is shown in the inset.

K which is the lowest temperature of this measurement, there is no anomaly corresponding to the magnetic order. These results indicate that the system of X=As goes into Kondo coherence state below about 15 K and results in the non-magnetic ground state, in contrast to X=Sb. The CF splitting estimated by the higher-T shoulder is about two times larger than that for X=Sb. This larger CF for X=As splitting could reflect slight enhancement of the anisotropy in $\chi(T)$ around 15 K. For X=As of ThCr$_2$Si$_2$-type, $\rho(T)$ shows a minimum around 20 K and increases with the decrease of the temperature down to T_N, revealing that this compound also belongs to the Kondo system, but T_K^{eff} could be below T_N. At higher temperatures, $\rho(T)$ shows the characteristic T-dependence like a broad bump around 200 K, corresponding to the anomaly due to the CF splitting. The estimated CF splitting is much larger than those for CaBe$_2$Ge$_2$-type and comparable to those of many other ThCr$_2$Si$_2$-type compounds [1] with the almost same ratio of the lattice parameter, a/c, as that of CeNi$_2$X$_2$.

From X=Sb to As for CaBe$_2$Ge$_2$-type with the decrease of the volume by 13%, T_K^{eff} is increased about six times. From the viewpoint of the substitution of Sb in CeNi$_2$Sb$_2$ by As, this increase of T_K^{eff} may result from the chemical pressure. The Gruneisen constant for T_K^{eff} can be obtained as $\Omega_{TKeff}\approx 13$, where Ω_{TKeff} is defined as $-(\delta \ln T_K^{eff}/\delta \ln V)$. This value of Ω_{TKeff} is relatively small, in spite of its small T_K [13]. For the present case, however, the substitution causes also the modification of the CF. The larger CF splitting for X=As decreases the effective degeneracy at the low temperature, leading to the decrease of T_K^{eff} [14] and the cancellation of the volume effect on T_K. Next, we compare both CeNi$_2$As$_2$, i.e. comparison between ThCr$_2$Si$_2$-type and CaBe$_2$Ge$_2$-type. T_K^{eff} for CaBe$_2$Ge$_2$-type is much larger than that for ThCr$_2$Si$_2$-type, although the volume of unit cell, the Ce–Ce distance, corresponding to a-axis, and the Ce–As distance for CaBe$_2$Ge$_2$-type are larger than those for ThCr$_2$Si$_2$-type. However, one of the Ce–Ni distance in CaBe$_2$Ge$_2$-type is the smallest one in all the distances between elements for both structures. Moreover, the Ni with this smallest distance locates not on the nearest basal Ni plane but on the second nearest one, giving the possibility to show less anisotropy than that for ThCr$_2$Si$_2$-type. Then, for CaBe$_2$Ge$_2$-type, it seems that the overlap between Ce–Ni dominates in the hybridization of the 4f electron, reflecting the Kondo effect and the CF. From X=As to P for ThCr$_2$Si$_2$-type with the decrease of the volume by only 8%, the system has been changed from the magnetic ground state to the intermediate valence. When this intermediate valence system is considered as the Kondo system with high T_K, the volume effect in this system corresponds to one with the highest sensitivity to the volume, giving $\Omega > 100$.

To summarize, the series of ternary pnictides CeNi$_2$X$_2$ have been investigated by the measurements of the magnetic susceptibility and the electrical resistivity, showing the variety of the relation among the Kondo effect, the inter-site magnetic interaction and the CF. In CaBe$_2$Ge$_2$-type, the characteristic energy scale of the Kondo effect increases with the decrease of the volume from X=Sb to As. $(T_N <) T_K < T_{CF}$ for both X=Sb and As, but the magnetic order appears for X=Sb, whereas the non-magnetic state due to the Kondo effect is realized for X=As. In ThCr$_2$Si$_2$-type, the system shows drastic change from the Kondo lattice with the magnetic ordering $(T_K < T_N << T_{CF})$ for X=As to the intermediate valence $(T_{CF} < T_K)$ for X=P.

Acknowledgements

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