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Electronic properties of $CeNi_4Si$ compound

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Temperature dependence of the specific heat for $CeNi_4Si$ was analyzed. These studies were supported by magnetic susceptibility, electrical resistivity and X-ray photoemission spectroscopy measurements. $CeNi_4Si$ is paramagnetic and follows the Curie–Weiss law with $\mu_{eff} = 0.52\ \mu_B$/f.u. and $\theta_P = -2$ K. This effective paramagnetic moment is lower than that for the free Ce^{3+}. The f-occupancy n_f and coupling Δ between the f level and the conduction state are derived to be about 0.91 and 36 meV, respectively. Both the susceptibility data and the XPS spectra have shown that Ce ions are in intermediate valence state. The specific heat has been analyzed considering the electronic contribution, the Schottky anomaly, and the lattice contributions within the Debye model. The scheme of the energy levels created by the crystal electric field split is determined from the Schottky contribution to the specific heat.

Key words: *XPS; specific heat of solids; mixed valence*

1. Introduction

The cerium based ternary compounds demonstrate various phenomena depending on the valence of the Ce ion. It is believed that the hybridization between the conduction electrons and 4f Ce electrons should be responsible for the valence state of Ce. A strong hybridization will decrease the localization of the 4f Ce electrons and result in a non-magnetic intermediate valence state. On the other hand, under a weak hybridization, the Ce 4f electrons become more localized, the localization resulting in a deeper position of the 4f levels.

In this paper, investigations of the specific heat of $CeNi_4Si$ are presented and supported by the magnetic susceptibility and X-ray photoemission spectroscopy (XPS).

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2. Experimental

The sample preparation was described in details in Refs. [1, 2]. The room temperature powder X-ray diffraction pattern revealed $CeNi_4Si$ to be a single phase [1]. Heat capacity measurements were performed by PPMS commercial device (Quantum Design) in the temperature range 2–300 K by relaxation method using the 2τ model.

3. Results and discussion

Our previous studies on $CeNi_4Si$ have revealed its paramagnetic properties with $\theta = -2$ K and $\mu_{eff} = 0.52\ \mu_B$/f.u [1]. However, the derived magnetic effective moment is much lower in comparison with free Ce^{3+} ions value equal to 2.54 μ_B. Since magnetic moment of tetravalent cerium is zero, the observed reduction of magnetic moment can be explained in a natural way by a fractional occupation of $4f^0$ (Ce^{4+}) and $4f^1$ (Ce^{3+}) configurations.

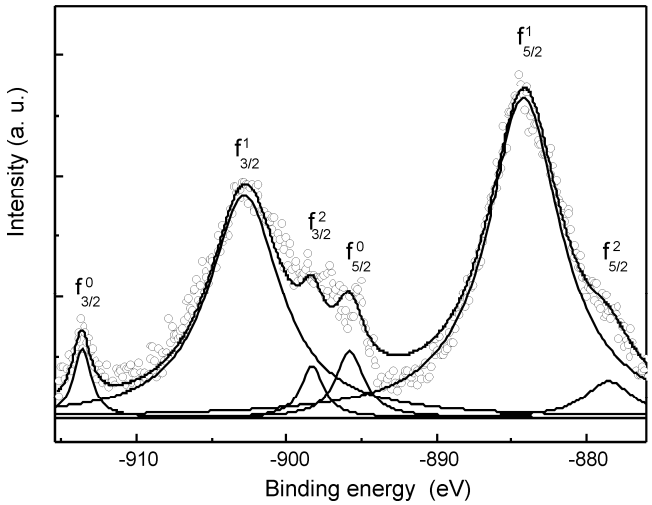

Fig. 1. Experimental XPS spectrum of the Ce($3d_{5/2,3/2}$) doublet for $CeNi_4Si$. A decomposition into main peaks and satellites is also displayed. The notation f^n corresponds to various XPS final states $3d^94f^n$

Figure 1 shows the Ce 3d core-level photoemission spectrum of $CeNi_4Si$. The spectrum exhibits two strong peaks at the binding energies –884.5 and –903.1 eV. These peaks are assigned to $3d_{5/2}$ and $3d_{3/2}$ spin-orbit components of the $3d^94f^1$ final states. It should be mentioned that numerous Ce-based intermetallics show three final states, f^0, f^1 and f^2. Since the ground state of Ce^{3+} ions has electronic configuration $4f^1$, the presence of both $4f^1$ and $4f^0$ states can indicate an intermediate valence character of the Ce ions. The analysis of the Ce (3d) peaks in the framework of the Gunnarsson

–Schönhammer model [3] provides information on the localization degree. The f occupancy n_f and coupling Δ between the f level and the conduction states are derived to be about 0.91 and 36 meV, respectively [1]. Hence, both the susceptibility and XPS spectra show that Ce ions in $CeNi_4Si$ are in an intermediate valence state.

Electrical resistivity of this compound is metallic [1]. Below 15 K, a shallow minimum in $\rho(T)$ is observed, typical of Kondo impurity systems. The increased ρ_0 (≈300 μΩ·cm) is mainly due to a random distribution of Ni(2) and Si on the 3g site. The total specific heat consists of electronic, phonon and magnetic contributions. The magnetic part includes both the contribution originating from the CEF excitations and the contributions due to the magnetic ordering.

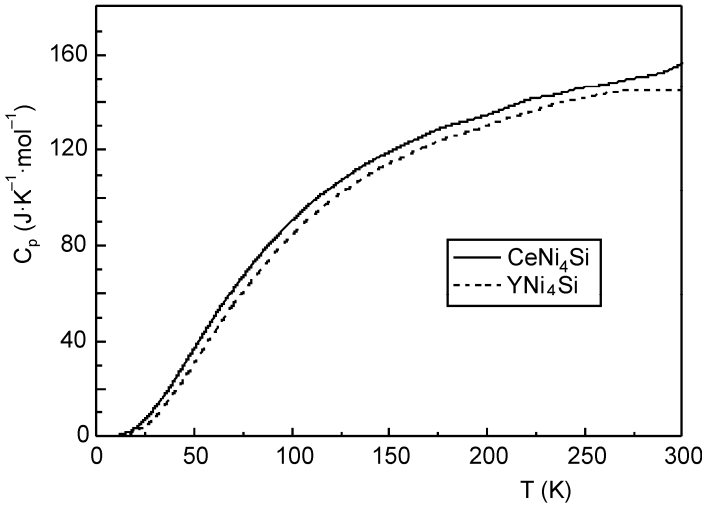

Fig. 2. Temperature dependence of the specific heat of $CeNi_4Si$ and YNi_4Si

Figure 2 shows the temperature dependence of the of the specific heat for YNi_4Si and $CeNi_4Si$ compounds. YNi_4Si is nonmagnetic; therefore, $C_p(T)$ can be described by the standard formula:

$$C_p(T) = \gamma T + 9NR\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x dx}{\left(e^x - 1\right)^2} \tag{1}$$

where the first and second term correspond to the electronic and the phonon contribution, respectively. $N = 6$ is the number of atoms in the formula unit and $x = \hbar\omega/k_BT$. From the fit to the experimental points (Fig. 2) we get the Debye temperature $\theta_D = 365$ K and the electronic specific heat coefficient $\gamma = 13$ mJ·mol^{-1}·K^{-2}. A similar analysis has been carried out for $CeNi_4Si$ yielding $\theta_D = 335$ K, $\gamma = 16$ mJ·mol^{-1}·K^{-2}.

To analyze the magnetic part of the specific heat of $CeNi_4Si$ we used the specific heat of the nonmagnetic isostructural analogue to get detailed information about the

electronic and phonon contributions. Figure 3 presents C_P/T vs. T for $CeNi_4Si$ after subtracting the specific heat of the YNi_4Si. The formula for the Schottky contribution is as follows [4, 5]:

$$C_{\mathrm{Sch}}(T) = \frac{R}{T^2}\left[\frac{\sum_{i=0}^{n-1} \Delta_i^2 \mathrm{e}^{-\Delta_i/T}}{\sum_{i=0}^{n-1} \mathrm{e}^{-\Delta_i/T}} - \left(\frac{\sum_{i=0}^{n-1} \Delta_i \mathrm{e}^{-\Delta_i/T}}{\sum_{i=0}^{n-1} \mathrm{e}^{-\Delta_i/T}}\right)^2\right] \tag{2}$$

where n denotes the number of the energy levels and $\Delta_0 = 0$. For Ce^{3+} ions, the 4f levels split into three doublets ($n = 3$).

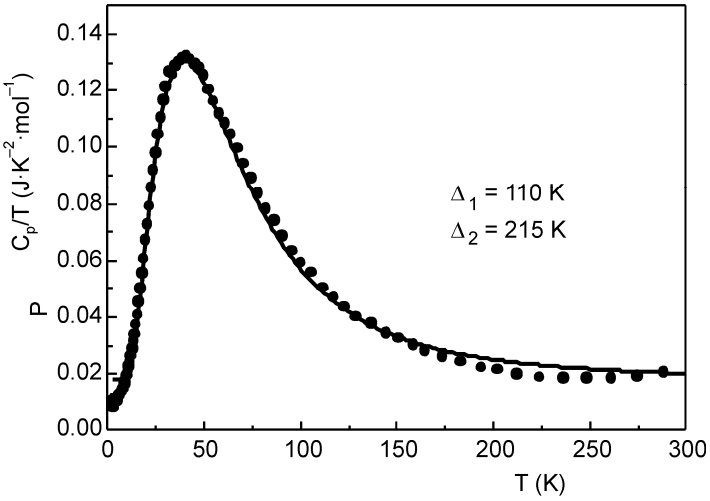

Fig. 3. Magnetic contribution to the specific heat obtained by subtracting the phonon and electronic contributions

The fit presented in Fig. 3 provides an estimate of the energy gaps: $\Delta_1 = 110$ K and $\Delta_2 = 215$ K.

The magnetic entropy

$$S_M = \int_0^T \frac{C_M(T)}{T}\, dT \tag{3}$$

is related to the degrees of freedom using the expression $S_{\mathrm{mag}} = R\ln(2J+1)$. For the Ce ion, the total angular momentum J is equal to 5/2 and consequently the expected value is $(2J + 1) = 6$. The entropy reaches the 100% value of $R\ln 2$ at $T = 62$ K. At room temperature, the entropy reaches 90% of $R\ln 6$.

The low temperature properties of many Ce- and Yb-based intermetallic compounds are well described within the Fermi liquid state. The specific heat C and the electrical resistivity ρ vary as a function of temperature as $C \propto \gamma T$ and $\rho \propto AT^2$. The coefficient γ and A are related to the electron effective mass m^* as $\gamma \propto m^*$ and $A \propto (m^*)^2$. Therefore, the ratio A/γ^2 does not depend on m^*. In fact, Kadowaki and Woods [6] showed that many Ce-based compounds (Fig. 4) show a universal relation $A/\gamma^2 = 1.0\times10^{-5}$ μΩ·cm·mol^2·K^2·mJ^{-2}. The value of the coefficient $A = 4\times10^{-3}$ μΩ·cm·K^{-2} has been obtained for $CeNi_4Si$ by fitting the resistivity data at low temperatures. The resulting A/γ^2 ratio for this compound is 1.5×10^{-5} μΩ·cm·mol^2·K^2·mJ^{-2}.

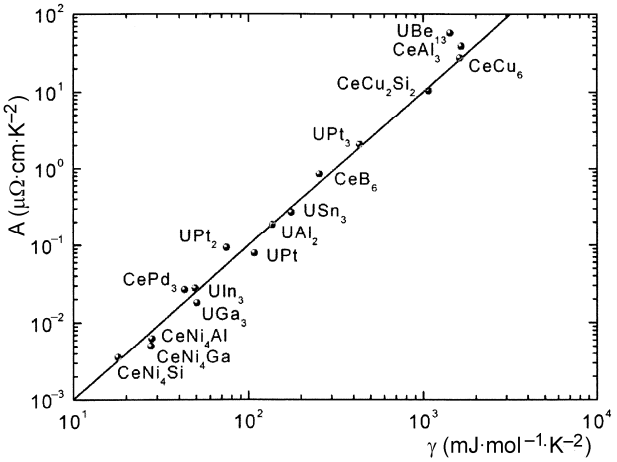

Fig. 4. Plot of the T^2 coefficient of the electrical resistivity, A vs. the T-linear specific heat coefficient γ. The results for $CeNi_4Si$, $CeNi_4Al$ and $CeNi_4Ga$ are added to the original plot of Kadowaki–Woods [6]

For a comparison, we show in Fig. 4 the values of the Kadowaki-Woods ratio, which we obtained for $CeNi_4Al$ ($A = 5\times10^{-3}$ μΩ·cm·K^{-2}, $\gamma = 29$ mJ·mol^{-1}·K^{-2}, and $A/\gamma^2 = 0.6\times10^{-5}$ μΩ·cm·mol^2·K^2·mJ^{-2}) and $CeNi_4Ga$ ($A = 4\times10^{-3}$ μΩ·cm·K^{-2}, $\gamma = 28.7$ mJ·mol^{-1}·K^{-2}, and $A/\gamma^2 = 0.5\times10^{-5}$ μΩ·cm·mol^2·K^2·mJ^{-2}). For the latter compound, the value of γ obtained from the ab initio TB LMTO calculations has been used [7]. It is visible from Fig. 4 that the values of A and γ do not classify the studied Ce-based compounds to the group of heavy fermions which occupy the upper part of the figure. Instead, they are located in the neighbourhood of the compounds known to show mixed valence behaviour (lower part of the figure).

4. Conclusions

$CeNi_4Si$ is paramagnetic and follows the Curie–Weiss law with $\mu_{eff} = 0.52$ μ_B/f.u. and $\theta_P = -2$ K. This effective paramagnetic moment is lower than that for free Ce^{3+}. The f-occupancy n_f and coupling Δ between the f level and the conduction states are

derived to be about 0.91 and 36 meV, respectively. Both the susceptibility data and the XPS spectra have shown that Ce ions are in intermediate valence state. The analysis of the Schottky peak appearing in the magnetic part of the specific heat has provided the scheme of the energy levels being a result of the splitting by the crystal electric field. For Ce, three Kramers doublets with $\Delta_0 = 0$, $\Delta_1 = 110$ K and $\Delta_2 = 215$ K have been obtained. The paramagnetic $CeNi_4Si$ was characterized by the $\gamma = 16$ $mJ \cdot mol^{-1}K^{-2}$ and $\theta_D = 335$ K.

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