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Journal of Alloys and Compounds 323–324 (2001) 431–434

Journal of ALLOYS AND COMPOUNDS

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Mixed valence state of Ce ions in $CeNi_2Al_3$

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Abstract

X-ray photoelectron spectroscopy (XPS) and magnetic susceptibility (χ) of $CeNi_2Al_3$ and of the reference compound YNi_2Al_3 are reported. Both valence band and core level spectra were analyzed. The $\chi(T)$ curve of $CeNi_2Al_3$ shows a maximum around 22 K, characteristic for the intermediate valence state of Ce ions, and at high temperatures obeys a Curie–Weiss law with an effective magnetic moment $\mu_{\mathrm{eff}} = 2.48\ \mu_B$/f.u. The Ce 3*d* and 4*d* XPS spectra have confirmed the mixed valence state of Ce ions in $CeNi_2Al_3$. The *f* occupancy n_f, and coupling Δ between the *f* level and the conduction states are derived to be about 0.85 and 80 meV, respectively.

Keywords: Intermetallics; Valence fluctuations; Magnetic measurements; X-ray photoelectron spectroscopy

1. Introduction

The intermetallic compound $CeNi_2Al_3$ crystallizes in the hexagonal structure of the $PrNi_2Al_3$ structure type with the lattice parameters $a = 5.309$ Å and $c = 4.045$ Å. The Ni–Ni distances in $CeNi_2Al_3$ and in the isostructural compound YNi_2Al_3 are very close to those in Ni metal. Magnetic properties of $CeNi_2Al_3$ were studied earlier by Cava et al. in the temperature range 4.2 K–300 K [1]. The abruptly decrease of the reciprocal susceptibility towards lower temperatures clearly evidences the presence of the magnetic impurities. These impurities hide in many cases the intrinsic properties of the samples, especially in the valence and spin fluctuation systems. The contribution of the magnetic impurities may be eliminated by analyzing for each temperature the field dependence of the magnetic susceptibility.

X-Ray Photoelectron Spectroscopy (XPS) has become a widely used technique for studying both the mixed valence state and the valence bands in rare earth–transition metal compounds. This method correlated with magnetic measurements provides informations regarding *f* occupancy n_f, the coupling Δ between 4*f* level and the conduction states, and the degree of localization of *d* electrons in Ce compounds with *d*-metals.

The aim of this paper is to study the valence state of Ce ions in $CeNi_2Al_3$ by analyzing the magnetic susceptibility and XPS spectra of this compound and of the reference compound YNi_2Al_3.

2. Experimental

The isostructural compounds $CeNi_2Al_3$ and YNi_2Al_3 were prepared by argon arc melting. The samples were melted repeatedly (four times) in the same atmosphere to ensure homogeneity. The weight losses of the final materials were found to be less than 1%. The purity of the starting material was 99.99% for Y and Al and 99.9% for Ce and Ni. X-ray powder diffraction measurements showed that the two compounds are single phases with the expected structure type.

Magnetic measurements were performed with a vibrating sample magnetometer in the temperature range 4.2–750 K and fields up to 90 kOe. For each temperature, the magnetic susceptibility has been determined from magnetization isotherms, according to a Honda–Arrott plot [2]:

$$\chi_m = \chi_i + cM_s/H \tag{1}$$

by extrapolation to $H^{-1} \rightarrow 0$. χ_m is the measured susceptibility, χ_i the intrinsic susceptibility, c the impurity content and M_s their saturation magnetization. A linear dependence of χ_m versus H^{-1} was evidenced for each temperature, showing that in the studied field range, saturation has been obtained.

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0925-8388/01/$ – see front matter
PII: S0925-8388(01)01104-5

The XPS spectra were recorded using a PHI 5600ci ESCA spectrometer with monochromatized Al K_α radiation at room temperature. The pressure in the ultra-high vacuum chamber was in the 10^{-10} mbar range during the measurements. Sample cleanliness was checked by monitoring the oxygen and carbon 1s levels.

3. Results and discussions

The magnetic susceptibility of YNi_2Al_3 is very small ($\chi \cong 0.6 \times 10^{-4}$ emu/mol) and almost constant over a large temperature range. As in many rare earth–nickel compounds, Ni in YNi_2Al_3 has no magnetic moment because of a charge transfer of valence electrons of Y and Al to the Ni 3*d*-band. The lack of any magnetic moment on the Ni sites in YNi_2Al_3 and $CeNi_2Al_3$ is also revealed by the valence bands. Fig. 1 shows the valence bands of the two compounds compared with that of Ni metal. The density of states at the Fermi level in YNi_2Al_3 and $CeNi_2Al_3$ is drastically reduced in comparison with pure Ni and the maximum of the valence bands is shifted to higher binding energy from 0.59 eV in Ni to 1.92 eV in YNi_2Al_3 and $CeNi_2Al_3$. The absence of the 6 eV satellite in the investigated compounds is another evidence of the complete filling of the 3*d*-band. The states at the Fermi level have 3*d* character in Ni metal and s–p character in YNi_2Al_3 and $CeNi_2Al_3$.

The intrinsic susceptibility of $CeNi_2Al_3$ as determined is shown in Fig. 2. The $\chi(T)$ curve shows a maximum around $T_{max} \cong 22$ K, characteristic for the intermediate valence state of Ce ions, and at high temperatures obeys a Curie–Weiss law modified by a temperature-independent part χ_0, according to:

$$\chi = C/(T - \theta) + \chi_0 \qquad (2)$$

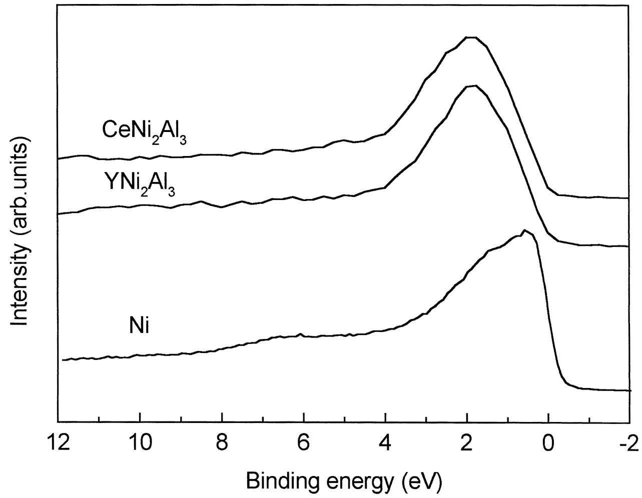

Fig. 1. XPS valence bands of $CeNi_2Al_3$, YNi_2Al_3 and Ni metal.

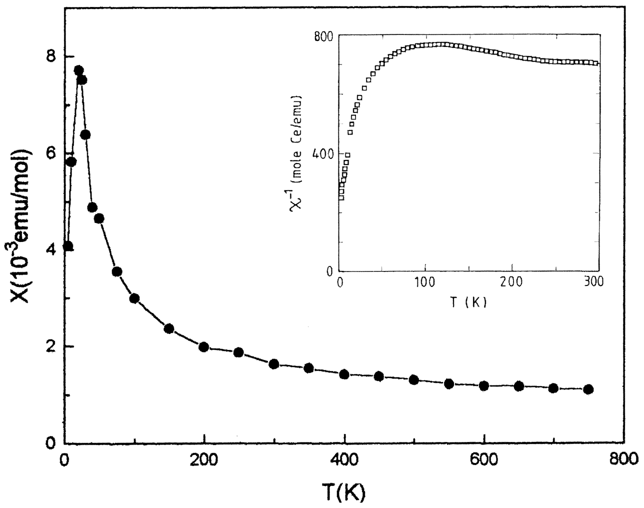

Fig. 2. Thermal variation of the susceptibility for $CeNi_2Al_3$. Inset: data taken from [1].

The thermal variation of the reciprocal susceptibility is linear in the temperature range 100–600 K, but shows a slightly deviation towards the temperature axis for $T > 600$ K due to temperature independent susceptibility χ_0, whose contribution to the total susceptibility becomes more important at higher temperatures. The paramagnetic Curie temperature is negative and very large, $\theta = -209$ K, and the effective magnetic moment determined from the Curie constant is $\mu_{eff} = 2.48\ \mu_B$/f.u., very close to the Ce^{3+} ion value (2.54 μ_B). The magnetic susceptibility measured by Cava et al. (see the inset) shows a broad minimum around 100 K and at lower temperatures increases rapidly with lowering temperature. The maximum in the $\chi(T)$ curve of $CeNi_2Al_3$ was hidden in the earlier investigation by the presence of the magnetic impurities. The low-temperature specific heat of $CeNi_2Al_3$ studied by the same authors confirmed this assumption [1]. The dependence C/T versus T shows a peak around 6.5 K from a small amount of impurity phase and an abruptly increasing at lower temperatures due to impurity spins.

The XPS spectra of the core levels 3*d* and 4*d* of Ce reflect the mixed valence in $CeNi_2Al_3$. In Fig. 3, the Ce 4*d* spectrum of $CeNi_2Al_3$, shows the multiplets arising from the interaction of the 4*d* hole with the 4f electrons, which are characteristic for all compounds with Ce in the trivalent state (the peaks corresponding to Ce^{3+} are superimposed on the Ni 3s peak at 111 eV), and two new peaks at binding energies 119.1 and 122.4 eV [3]. The Al 2s peak at 118 eV partly overlaps the Ce 4*d* peak at 119 eV. The last two peaks correspond to the fraction of tetravalent Ce in $CeNi_2Al_3$. The spin–orbit splitting is 3.3 eV, in good agreement with the value of 3.2 eV measured in the spectrum of the mixed valence compound CeF_4 [4].

The Ce 3*d* spectrum of $CeNi_2Al_3$ shows a superposition of spin–orbit-split peaks corresponding to the two initial

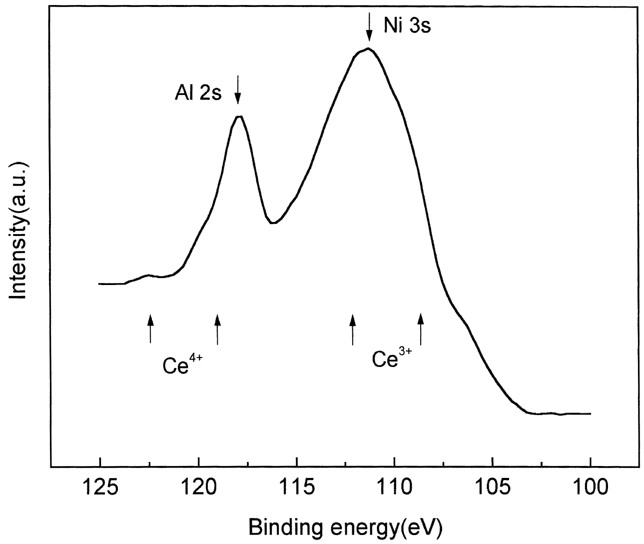

Fig. 3. XPS spectrum of the Ce 4*d* level in $CeNi_2Al_3$.

configurations Ce^{3+} and Ce^{4+} (Fig. 4). The spin–orbit splitting is 18.5 eV. Multiplet effects due to the coupling of the 3*d* hole with the open 4*f* shell are visible in both $3d_{3/2}$ and $3d_{5/2}$ peaks. There is clear evidence of a $3d^9 4f^0$ component at 914.6 eV which is not present in compounds with all Ce ions in the trivalent state. The intensity of the $3d^9 4f^2$ final-state component is also increased in comparison with that in Ce trivalent compounds. These findings again indicate the mixed valence state of Ce ions in $CeNi_2Al_3$.

In order to estimate the *f* occupancy, n_f, and the coupling, Δ, between the *f* level and the conduction states, we used the expressions:

$$\chi_{Ce}(0) = \pi j(j+1) g_j^2 \mu_B^2 n_f^2 / 3\Delta(2j+1)(1-n_f) \qquad (3)$$

and

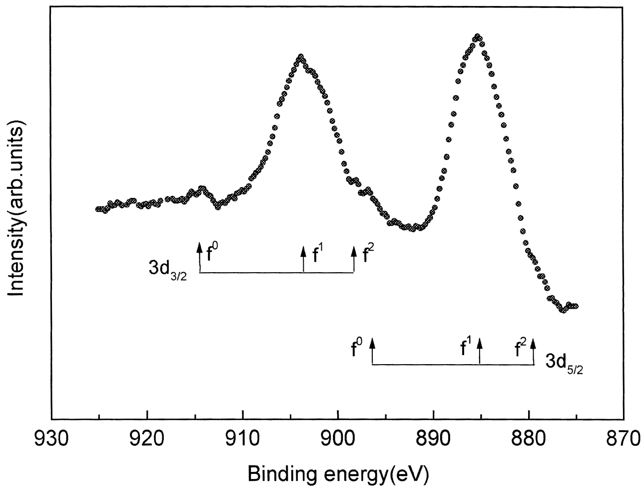

Fig. 4. XPS spectrum of the Ce 3*d* level in $CeNi_2Al_3$.

$$1 - n_f = (\pi B/N_f\Delta)\exp(\pi\epsilon_f/N_f\Delta) \qquad (4)$$

deduced by Gunnarsson and Schönhammer for Ce compounds with a nonmagnetic ground state [5]. The extrapolated Ce magnetic susceptibility at $T \to 0$ K may be obtained from the difference $\chi_{Ce} = \chi(CeNi_2Al_3) - \chi(YNi_2Al_3)$ and has the value $\chi_{Ce}(0) = 36.72 \times 10^{-28}$ emu/Ce atom. In Eqs. (3) and (4), $j = 5/2$, $g_j = 6/7$, B is the total valence bandwidth, N_f is the degeneracy of the *f* level and ϵ_f is the 4*f* energy position below the Fermi level. With $B = 4.8$ eV, the measured bandwidth in $CeNi_2Al_3$ (see Fig. 1), and $\epsilon_f = -1.6$ eV, a common value used also in [5] for Ce mixed valence compounds, we obtained $n_f \cong 0.85$ and $\Delta \cong 0.80$ meV, in good agreement with the values found for mixed valence compounds [6].

4. Conclusions

Summarizing the results, one may conclude from both susceptibility data and XPS spectra that Ce ions in $CeNi_2Al_3$ are in the intermediate valence state. The correlation of the data obtained from the two kind of measurements gives the possibility to estimate the *f* occupancy, n_f, and the coupling, Δ, between the *f* level and the conduction states in Ce mixed valence compounds.

As in many rare earth–nickel compounds, the lack of any magnetic moments on the Ni sites in YNi_2Al_3 and $CeNi_2Al_3$ may be attributed to the charge transfer from Y and respectively Ce to the Ni–3*d* band. On the other hand, the transfer of Ce 5*d* electrons to the Ni–3*d* band lowers E_F in $CeNi_2Al_3$ compared to E_F of pure Ce and renders the hybridization favorable, driving Ce to a mixed valence state [7].

The present investigation, in conjunction with earlier studies on ACo_2 (A=Y, Lu, Zr, Sc, and Hf) [8,9] and YNi_5 and $CeNi_5$ [10], serve to show that impurities and defects in many rare earth–transition metal compounds can alter in a large measure the intrinsic properties of these compounds. This effect is more pronounced in the valence and spin fluctuations systems, at which the low-temperature susceptibilities are smaller than that of the magnetic impurities. In order to avoid a possible alteration of the magnetic susceptibilities caused by the presence of magnetic impurities, the values of the magnetic susceptibility should be obtained from magnetization isotherms, by extrapolation to $H^{-1} \to 0$.

Acknowledgements

One of us (M.C.) would like to thank the Alexander von Humboldt Foundation for financial support and the University of Osnabrück for the kind hospitality.

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