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Evidence for Kondo-type behaviour in $\text{Ce}_x\text{R}_{1-x}\text{M}$ compounds with $\text{R} = \text{La}, \text{Y}$ and $\text{M} = \text{Mg}, \text{Zn}$

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Résumé. — Les composés CeMg , CeZn et leurs solutions diluées $\text{Ce}_x\text{R}_{1-x}\text{M}$ avec $\text{R} = \text{La}, \text{Y}$ et $\text{M} = \text{Mg}, \text{Zn}$ ont une structure cristallographique du type CsCl . Les propriétés magnétiques et électriques des composés dilués ont été mesurées entre 1,5 et 300 K. Les susceptibilités paramagnétiques ont un comportement de Curie-Weiss avec des constantes de Curie proches de celle de l'ion libre trivalent à haute température. À plus basse température apparaissent des déviations dues au champ cristallin et à l'effet Kondo. On observe des minima de résistivité dans les composés $\text{Ce}_{0,2}\text{Y}_{0,8}\text{Mg}$, $\text{Ce}_{0,1}\text{Y}_{0,9}\text{Mg}$ et $\text{Ce}_{0,05}\text{Y}_{0,95}\text{Zn}$. Les coefficients électroniques γ ont été déduits des mesures de chaleur spécifique de CeMg et CeZn . Leurs valeurs respectivement de 40 ± 10 et $19 \pm 5 \text{ mJ/mole K}^2$ sont beaucoup plus fortes que celles des matrices non magnétiques correspondantes.

Abstract. — The compounds CeMg , CeZn and the dilute solutions $\text{Ce}_x\text{R}_{1-x}\text{M}$ with $\text{R} = \text{La}, \text{Y}$ and $\text{M} = \text{Mg}, \text{Zn}$ have the CsCl -type structure. The magnetic and electrical properties of the dilute compounds were investigated in the temperature range 1.5-300 K. The paramagnetic susceptibilities show Curie-Weiss behaviour with Curie constants close to the free ion value at high temperatures, but show at lower temperatures deviations due to crystal field and Kondo effects. Resistivity minima are observed in $\text{Ce}_{0,2}\text{Y}_{0,8}\text{Mg}$, $\text{Ce}_{0,1}\text{Y}_{0,9}\text{Mg}$ and $\text{Ce}_{0,05}\text{Y}_{0,95}\text{Zn}$. The electronic coefficients γ are deduced from the specific heat measurements on CeMg and CeZn . These values respectively 40 ± 10 and $19 \pm 5 \text{ mJ/mole K}^2$ are much higher than the corresponding values for non-magnetic matrices.

1. Introduction.

CeMg and CeZn compounds exhibit a trivalent cerium state and order antiferromagnetically at 19.5 K and 29.5 K respectively. Some of their properties may indicate a Kondo-type behaviour: the magnetic resistivities decrease at high temperatures [1]. The Néel temperatures decrease with increasing hydrostatic pressure [2]; the relative variation of T_N , $d \ln(T_N)/dp$ is similar to that found in CeAl_2 and CeIn_3 [3, 4]. However, the rather high Ruderman-Kittel interactions somewhat blur the one-ion properties and prevent the characteristic low temperature anomalies such as resistivity minima from being observed. In order to separate local one-ion properties from interactions or coherence effects, we have studied the magnetic properties and electrical resistivity of some dilute compounds such as $\text{Ce}_x\text{R}_{1-x}\text{M}$ with $\text{R} = \text{La}, \text{Y}$ and $\text{M} = \text{Mg}, \text{Zn}$.

2. Crystallographic properties.

CeMg , CeZn and their dilute solutions have a CsCl -type structure with lattice parameters given in table I.

No significant deviation from Vegard's law is observed for the lattice parameters. For compounds diluted with yttrium, we expect a rather large « chemical pressure » at the cerium site.

3. Magnetic properties.

Magnetic measurements were made on polycrystalline samples between 1.5 and 300 K using a superconducting coil. Isothermal magnetization curves were obtained at 1.5 and 4.2 K in fields up to 75 kOe. In all cases the magnetization, M , remains linear in fields lower than 10 kOe (Fig. 1). Thus the susceptibility was measured in the temperature range 1.5-300 K in fields smaller than 10 kOe. In order to obtain the susceptibility of the cerium ions, the experimental measurements are corrected by subtraction of the related non-magnetic matrix (LaM or YM) [5, 6].

In both series the corrected susceptibilities follow a Curie-Weiss law (Fig. 2) from 50 to 300 K with Curie constants close to the free ion value. Due to the relative magnitude of the corrections, the deviations from the free ion Curie constant value are not fully

Table I. — Lattice parameters a , effective paramagnetic moments μ_{eff} measured at low (LT) and high (HT) temperatures, paramagnetic Curie temperatures θ_p for RMg and RZn compounds.

Compounds	a (Å)	$\mu_{\text{eff}}(\text{LT})$ (μ_B)	$\mu_{\text{eff}}(\text{HT})$ (μ_B)	$\theta_p(\text{LT})$ (K)
YMg	3.79 ± 0.005	—	—	—
LaMg	3.96 ± 0.005	—	—	—
$\text{Y}_{0.9}\text{Ce}_{0.1}\text{Mg}$	3.80 ± 0.005	2.33 ± 0.05	2.40 ± 0.1	-3 ± 0.5
$\text{Y}_{0.8}\text{Ce}_{0.2}\text{Mg}$	3.81 ± 0.005	2.37 ± 0.05	2.63 ± 0.1	-3 ± 0.5
$\text{La}_{0.8}\text{Ce}_{0.2}\text{Mg}$	3.95 ± 0.005	2.48 ± 0.05	2.55 ± 0.1	-2 ± 0.5
CeMg	3.90 ± 0.005	2.50 ± 0.05	2.54 ± 0.1	-3 ± 0.5
YZn	3.57 ± 0.005	—	—	—
LaZn	3.76 ± 0.005	—	—	—
$\text{Y}_{0.95}\text{Ce}_{0.05}\text{Zn}$	3.58 ± 0.005	2.01 ± 0.05	2.40 ± 0.1	-1 ± 0.5
$\text{Y}_{0.8}\text{Ce}_{0.2}\text{Zn}$	3.60 ± 0.005	2.00 ± 0.05	2.52 ± 0.1	$+4 \pm 0.5$
$\text{La}_{0.8}\text{Ce}_{0.2}\text{Zn}$	3.74 ± 0.005	2.14 ± 0.05	2.51 ± 0.1	-1 ± 0.5
CeZn	3.70 ± 0.005	2.20 ± 0.05	2.45 ± 0.1	$+11 \pm 2$

Fig. 1. — Magnetization curves up to 75 kOe at 1.5 and 4.2 K for $\text{Y}_{0.9}\text{Ce}_{0.1}\text{Mg}$, $\text{La}_{0.8}\text{Ce}_{0.2}\text{Mg}$, $\text{Y}_{0.8}\text{Ce}_{0.2}\text{Zn}$ and $\text{La}_{0.8}\text{Ce}_{0.2}\text{Zn}$. The full lines in part (a) represent the theoretical magnetization for $\text{Y}_{0.9}\text{Ce}_{0.1}\text{Mg}$ in fields along [001], [011] and [111] for the case of a Ce^{3+} ion with Γ_8 ground state.

significant. Under 50 K, significant deviations from Curie-Weiss behaviour are observed, which are mainly attributed to crystal field (CF) effects. The crystal field splitting has been previously determined from inelastic neutron scattering in CeZn [1] and CeMg [7]. Both compounds have a Γ_8 ground state, with crystal field splitting $\Delta_{\text{CF}} = 60$ and 190 K respectively. The overall reciprocal susceptibility for $\text{Ce}_x\text{R}_{1-x}\text{Mg}$ compounds is well described with $\Delta_{\text{CF}} = 190$ K (Fig. 2), but it is necessary to increase significantly the crystal field parameter (up to $\Delta \approx 300$ K) in order to describe

Fig. 2. — Reciprocal magnetic susceptibilities for $\text{Y}_{0.8}\text{Ce}_{0.2}\text{Mg}$ and $\text{Y}_{0.8}\text{Ce}_{0.2}\text{Zn}$. The values are corrected for the non-magnetic matrix contribution. Continuous lines are fits taking into account crystal field splitting Δ_{CF} .

the susceptibility of $\text{Ce}_x\text{Y}_{1-x}\text{Zn}$ compounds. Inelastic neutron scattering performed on $\text{Ce}_{0.2}\text{Y}_{0.8}\text{Zn}$ (to be published) shows a broad inelastic spectrum extending up to 20 meV, whereas the spectra for $\text{Ce}_{0.2}\text{La}_{0.8}\text{Zn}$ showed [7] a well-defined crystal field excitation at 5.5 meV. Thus dilution by yttrium possibly enhances the crystal field parameter in the RZn series.

The effective moments calculated from the inverse susceptibility at low temperature (Fig. 3, Table I) are close to the expected value for the Γ_8 ground state ($2.0 \mu_B$) in $\text{Ce}_x\text{R}_{1-x}\text{Zn}$ solutions. However, in the $\text{Ce}_x\text{R}_{1-x}\text{Mg}$ series, the experimental values are higher. The susceptibility is then « more flat » than it should be. The reduction of the low temperature susceptibility is also obvious from the negative values of the asymptotic Curie-Weiss temperatures θ_p (Table I). For $\text{Ce}_x\text{R}_{1-x}\text{Mg}$ series, it remains negative and approximately independent of the concentration; thus it does not arise from Ruderman-Kittel type interactions, but rather from local Kondo couplings. The susceptibility is then $\chi = C/(T + T_K)$ with a Kondo temperature $T_K \sim 3$ K.

For CeZn , overall Ruderman-Kittel interactions are strongly positive (Table I). With dilution, θ_p decreases from 11 K in CeZn to -1 K in $\text{Ce}_{0.05}\text{Y}_{0.95}\text{Zn}$ and -1 K in $\text{Ce}_{0.2}\text{La}_{0.8}\text{Zn}$, showing a tendency to negative values in the most diluted solutions. An interesting case is $\text{Ce}_{0.2}\text{Y}_{0.8}\text{Zn}$, where in spite of a positive θ_p value the susceptibility flattens and does not diverge. This could be due to spin-glass effects, but thermal cycling between 1.5 and 20 K shows no hysteresis, contrary to the case of spin glasses. Thus the flattening of the susceptibility may be related to

the decrease of the magnetic moment at low temperatures, as revealed by the following magnetization behaviour.

Magnetization curves at 1.5 and 4.2 K are shown in figure 1. Clearly these magnetization curves do not follow a Brillouin-like curve corresponding to the full Γ_8 quartet moment. In order to trace the discrepancy, we have drawn, as full lines on figure 1a, the theoretical magnetization expected for $\text{Ce}_{0.1}\text{Y}_{0.9}\text{Mg}$ on the basis of the measured initial susceptibility. These curves are given for 1.5 and 4.2 K and for a field along [001], [011] and [111] symmetry directions respectively, taking into account the experimental value of θ_p . The experimental magnetization in high field is about 25 % lower than that calculated in this case; the reduction of the moment is even larger for $\text{Ce}_{0.2}\text{Y}_{0.8}\text{Zn}$.

All these phenomena indicate a screening of the local moment by conduction electrons. The screening — or the Kondo interaction — is larger in Y-diluted than in La-diluted systems, as theoretically expected from the enhancement of the mixing parameter J with decreasing volume. The Kondo temperature of (R, Ce) Mg compounds has been recently estimated in a different way by inelastic neutron scattering [8]. In these experiments, the residual width of the quasi-elastic line of the spectrum is expected to be related to the energy of spin fluctuations — or to the Kondo temperature [9]. From these data, T_K should be of the order of 5 K in CeMg and $\text{La}_{0.8}\text{Ce}_{0.2}\text{Mg}$, and increase up to about 10 K in $\text{Y}_{0.8}\text{Ce}_{0.2}\text{Mg}$. These values are in qualitative agreement with susceptibility data. Similar observations have been performed in other systems, such as $\text{R}_{1-x}\text{Ce}_x\text{Al}_2$ [10].

4. Electrical resistivity.

The resistivity of all samples was measured between 1.7 and 300 K using a four-probe method with a.c. current. The absolute error on the resistivity is estimated to be less than 2 %.

Experiments on diluted systems reveal the existence of resistivity minima in $\text{Y}_{0.8}\text{Ce}_{0.2}\text{Mg}$ ($T_{\min} = 25 \pm 2$ K), $\text{Y}_{0.9}\text{Ce}_{0.1}\text{Mg}$ ($T_{\min} = 23 \pm 2$ K) and $\text{Y}_{0.95}\text{Ce}_{0.05}\text{Zn}$ ($T_{\min} = 18 \pm 3$ K) (Figs. 4 and 5). Below 10 K, the positive slope of the resistivity in $\text{Y}_{0.8}\text{Ce}_{0.2}\text{Mg}$, $\text{La}_{0.8}\text{Ce}_{0.2}\text{Mg}$ and $\text{La}_{0.8}\text{Ce}_{0.2}\text{Zn}$ may be due to ordering effects; we note however, that these effects are not evident from the susceptibility measurements. For $\text{Y}_{0.8}\text{Ce}_{0.2}\text{Zn}$ the resistivity becomes constant below 40 K. This may again be characteristic of spin glass behaviour, but such behaviour is often observed in diluted Kondo systems.

The magnetic contribution ρ_m to the resistivity (Figs. 6, 7) is obtained by subtracting the resistivity of the corresponding La or Y compound. As for pure CeMg and CeZn [1], it shows a linear decrease as a function of the logarithm of temperature above 150 K, the slope being roughly proportional to the Ce concentration. For CeMg , the parameter $Jn(E_F)$ was

Fig. 3. — Reciprocal magnetic susceptibilities in the low temperature range. Full lines correspond to theoretical values for Γ_7 , Γ_8 ground state or free Ce^{3+} ion.

Fig. 4. — Electrical resistivities for $\text{La}_{1-x}\text{Ce}_x\text{Mg}$ and $\text{Y}_{1-x}\text{Ce}_x\text{Mg}$ compounds.

Fig. 5. — Electrical resistivities for $\text{Y}_{1-x}\text{Ce}_x\text{Zn}$ compounds.

evaluated following the theory of Cornut and Coqblin [11] for Kondo Ce impurities submitted to crystal fields, and a value of -0.045 was obtained. For diluted systems, there is an additional temperature

Fig. 6. — Magnetic resistivity of $\text{Y}_{0.8}\text{Ce}_{0.2}\text{Zn}$ versus temperature (logarithmic temperature scale). The magnetic resistivity is obtained by subtracting the YZn resistivity.

Fig. 7. — Magnetic resistivities of CeMg , $\text{La}_{0.8}\text{Ce}_{0.2}\text{Mg}$ and $\text{Y}_{0.8}\text{Ce}_{0.2}\text{Mg}$ (logarithmic temperature scale). The magnetic resistivities are obtained by subtracting that of LaMg for CeMg and $\text{La}_{0.8}\text{Ce}_{0.2}\text{Mg}$, and the YMg resistivity for $\text{Y}_{0.8}\text{Ce}_{0.2}\text{Mg}$.

independent term from incoherent Coulomb scattering [11]; it contributes to the residual resistivity and is responsible for the huge values found in $\text{Y}_{1-x}\text{Ce}_x\text{Mg}$ and $\text{Y}_{1-x}\text{Ce}_x\text{Zn}$ solutions. It also prevents a precise determination of $Jn(E_F)$ for diluted systems. However, as the negative slope of ρ_m versus $\ln(T)$ scales with the concentration in $(\text{R}, \text{Ce})\text{Mg}$ solutions, we expect that $Jn(E_F)$ does not depend much on dilution.

5. Specific heat and density of states.

The specific heat was measured for pure La and Ce compounds using a continuous heating method. The experiments were performed at the Service des Basses Températures of the Centre d'Etudes Nucléaires of Grenoble. Some results have already been published on YMg [12], LaMg and CeMg [7]. We summarize here the results concerning the electronic coefficient γ of the specific heat (Table II). The γ term has the same order of magnitude in LaMg , YMg , LaZn and

Table II. — *Electronic contribution to the specific heat γ and Pauli susceptibility extrapolated to 0 K, χ_0 in some pure compounds.*

	γ (mJ/mole K ²)	χ_0 (e.m.u./mole)
LaMg	6.8 ± 0.1 [7]	0.27×10^{-4} [5]
YMg	7.8 ± 0.1 [12]	1.92×10^{-4} [5]
CeMg	40 ± 10	—
LaZn	9 ± 1.5	0.24×10^{-4} [6]
YZn	7.3 [13]	1.9×10^{-4}
CeZn	19 ± 5	—

YZn. In the case of YMg and YZn [13], this magnitude is well explained by the occurrence of a large density of d-states at the Fermi level, and is in agreement with the values of the paramagnetic Pauli susceptibility [5]. Conversely, the measured Pauli susceptibility is lower for LaZn [6] and LaMg [5].

Some magnetic impurities are present in our samples. Besides cerium oxide — present in nearly all inter-metallic compounds —, CeMg contains a few percent of CeMg_3 , which gives a specific heat anomaly below 4 K, whereas CeZn contains probably CeZn_2 , giving an extra peak near 7 K. Nevertheless, the γ coefficient (Table II) may be deduced with sufficient confidence in these two compounds, eliminating the temperature ranges where anomalies occur (Fig. 8). The slope of the C/T versus T^2 plot is mainly due to T^3 terms from antiferromagnetic spin wave excitations. The plots for LaMg and LaZn show a positive curvature above 6 K; assuming such a curvature to be present in CeMg would give a slightly higher γ term. Obviously, CeZn and CeMg have higher γ terms than the corresponding non-magnetic matrices, proving some influence of f electrons on the density of states at the Fermi level.

6. Discussion.

We shall first comment on the magnetic measurements. At high temperatures all the studied solutions follow Curie-Weiss laws with Curie constants close to that of free trivalent ion. Low temperature data show deviations which are partly explained by crystal field effects corresponding to a Γ_8 ground state, but the experimental susceptibility is less than that predicted with the crystal field model. This reduction may be

Fig. 8. — Plot of C/T versus T^2 for CeMg, LaMg, CeZn and LaZn.

related to Kondo temperatures of the order of a few Kelvins. The occurrence of a Kondo effect also explains the reduced magnitude of the magnetization at low temperatures.

Resistivity minima and the negative slope of the magnetic part of the resistivity are unambiguous signatures of Kondo-type couplings. The coupling parameter $Jn(E_F)$ is of the order -0.05 , close to that found for instance in CeAl_2 [11]. The electronic contribution to the specific heat is larger for CeMg and CeZn compounds than for LaMg and LaZn. This contribution however is much less than that observed in most cerium compounds; in our case it was measured in the ordered range, where the spin fluctuation contributions are suppressed by the exchange field.

In summary, the present study confirms that CeMg and CeZn are Kondo lattices with a fourfold degenerate ground state in the paramagnetic range. Due to their simple crystallographic and magnetic structures, they are good candidates for the study of interactions and magnetic excitations in a Kondo lattice.

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