Interconfigurational fluctuations in Ce cubic compounds

J. Sereni, G. Olcese, C. Rizzuto

To cite this version:

J. Sereni, G. Olcese, C. Rizzuto. Interconfigurational fluctuations in Ce cubic compounds. Journal de Physique Colloques, 1979, 40 (C5), pp.C5-337-C5-339. 10.1051/jphyscol:19795116 . jpa-00218900

JOURNAL DE PHYSIQUE *Colloque* C5, *supplément au n*° 5, *Tome* 40, *Mai* 1979, *page* C5-337

Interconfigurational fluctuations in Ce cubic compounds

J. G. Sereni (*) (**)

Centro Atòmico Bariloche (CNEA), Bariloche, Argentina

G. L. Olcese

Istituto di Chimica Fisica, Università di Genova, Italia

and C. Rizzuto

Istituto di Scienze Fisiche, Università di Genova, Italia

Résumé. — La susceptibilité magnétique de trente composés cubiques de cérium est analysée, en supposant une dépendance en température des fluctuations de valence. Le schéma des niveaux d'énergie obtenu par l'ajustement de la susceptibilité mesurée est utilisé pour calculer d'autres propriétés physiques. On a trouvé une corrélation entre le rayon ionique du cérium et l'énergie d'excitation interconfigurationnelle.

Abstract. — The magnetic susceptibility of thirty Ce cubic compounds is analyzed, assuming a temperature dependence of the valence fluctuations. The energy level scheme, obtained by fitting the measured susceptibility is used to calculate other physical properties. A correlation between the Ce ionic radius and the interconfigurational excitation energy has been found.

The magnetic susceptibility (MS) of thirty Ce cubic intermetallic compounds (IC), of different crystal structures (see the table I), which shows magnetic, intermediate and non magnetic behaviours, has been analyzed assuming a temperature dependence of the valence fluctuations. We have applied the concept of interconfigurational fluctuations (ICF) [1, 2] to describe the observed temperature dependence of the MS [3], taking into account the possibility of a dynamical mixing between the two lower energy Ce configurations ($4f^1\,5d^1 \rightleftharpoons 4f^0\,5d^2$), identified as $n = 1$ and $n - 1 = 0$ respectively. From this model we have derived a sufficiently accurate energy level scheme to attempt to fit available experimental data of different physical properties.

The probability of occupation of the state « n » (of energy E_n and width Δ_n), is given at $T \to 0$ by : $P_n(0) \sim \exp(-E_n/\Delta_n)$, and at high temperatures by : $P_n(T) \sim \exp(-E_n/k_b T)$. A good interpolation is done considering $P_n(T) \sim \exp(-E_n/T_n)$ [4], where $T_n = T + \Delta_n$, and $k_b = 1$ using K as energy unit. So, the valence dependence with temperature was taken as the *fractional occupation* of the configuration $4f^1\,5d^1$ ($n = 1$), i.e.

$$V(T) = 1/Z \int_{-\infty}^{\infty} D_n(E)\, f_n^x(E)\, \mathrm{d}E\,,$$

where $f_n^x(E) = \exp(-E_n/T_n)$ is the quasi Boltzmann distribution and « Z » the partition function,

$$Z = \sum_n (2\,J_n + 1)\, f_n^x(E)\,.$$

Taking $D_n(E) \sim \exp[-(E - E_n)^2/2\,\Delta_n^2]$ it is possible to integrate, obtaining :

$$V(T) = (2\,J_n + 1) \exp[\tfrac{1}{2}(\Delta_n/T_n)^2 - E_n/T_n]\,.^1/z\,.$$

Substituting T by T_n, the MS can be written as $\chi(T) = (N/3\,T_n).\sum_n \mu_n^2\, V(T)$. In the case of Ce it is : $\mu_1 = 2.54\,\mu_B$ and $\mu_0 = 0$. To apply this expression to a real case, it is necessary first to account for other effects, which will be considered as independent from ICF. They are : 1) The possible interactions between magnetic moments, which give rise to a Curie-Weiss temperature (T_0), 2) the Van Vleck contribution to the MS, independent from temperature, and 3) the possible splitting, into a doublet Γ_7 and a quarted Γ_8, of the Hund sixfold ground state due to the crystal field effect. These exchange interactions will be represented by $|\langle \Gamma_i | J_z | \Gamma_j \rangle| = J_{ij}$. Under these considerations the general expression for the MS becomes :

$$\chi(T) = N g_n^2\, \mu_B^2/Z \left\{ \left[\sum_{i,j} \left(\frac{J_{ii}^2}{T_n - T_0} + \frac{2\,J_{ij}^2}{E_j - E_i} \right) \exp(-E_{n_i}/T_{n_i}) \right] + \frac{2\,J_{nn'}^2}{E' - E_n} \exp(-E'/T) \right\}$$

(*) Supported in part by the GNSM-CNR.

(**) Present address : II Physikalisches Institut der Universität zu Köln, Zülpicher Strasse 77, 5 Köln 41, Germany.

Table I.

Compound	Structure type	Lattice parameter (Å)	Ce ionic radius (Å)	E_{ex} (K)	Magnetic behaviour	Specific heat calc. (mJ/K mole)	Specific heat meas. (mJ/K mole)
$CeSn_3$	$AuCu_3$	4.722	1.013	− 190	Intermed.	64	53
$CePd_3$		4.163	1.009	− 360		29	36
$CeRh_3$		4.025	0.980	− 1 600			
$CeTl_3$		4.771	1.034	850	Magnetic		
$CeIn_3$		4.691	1.034	$E_{ex} > E'$			
$CePb_3$		4.875	1.025	550			
Ce_3Al		5.013	1.020	$E_{ex} > E'$	Magnetic		
Ce_3Ga		5.115					
Ce_3In		5.061	1.040				
$CeNi_2$	$MgCu_2$	7.208	0.954	− 470	Non mag.	10.3	25.6
$CeRu_2$		7.543	0.920	− 1 260		33	30
$CeRh_2$		7.546	0.977	− 420			
$CeOs_2$		7.593	0.938	− 430			
$CeIr_2$		7.576	0.964	− 910			
$CePt_2$		7.741	1.034		Magnetic		
$CeAl_2$		8.060	1.030	$E_{ex} > E'$	Magnetic		
CeN	NaCl	5.022	0.955	− 2 150	Non mag.	0	8
CeP		5.913	1.020	520	Magnetic		
CeAs		6.086	1.037	1 160			
CeSb		6.429	1.032	700			
CeBi		6.505	1.031	860			
CeAg	CsCl	3.736	1.032	$E_{ex} > E'$	Magnetic		
CeMg		3.924	1.034				
CeZn		3.713	1.030				
CeHg		3.808	1.030				
CeTl		3.893	1.033				
$CeCd_3$	$BiLi_3$	7.218		$E_{ex} > E'$	Magnetic		
$CeBe_{13}$	$NaZn_{13}$	10.375	1.020	− 320	Intermed.	95	115
CeB_6	CaB_6	4.140	1.022	− 80	Intermed.		
Ce_2C_3	Pu_2C_3	8.447	0.952	− 1 200	Non mag.		

where $g_n = 6/7$ and E' is the energy of the first J-excited level characterized by $J' = 7/2$. The level scheme was obtained by fitting this formula to the actual experimental data [3].

In table I we give the values of the excitation energy between configurations : $E_{ex} = E_{n-1} - E_n$, obtained from this method, as well as the comparison between the calculated and the measured *specific heat* values at $T = 1$ K for some compounds. The calculated *thermoelectric power* of $CeSn_3$ and $CeBe_{13}$ [5], *nuclear*

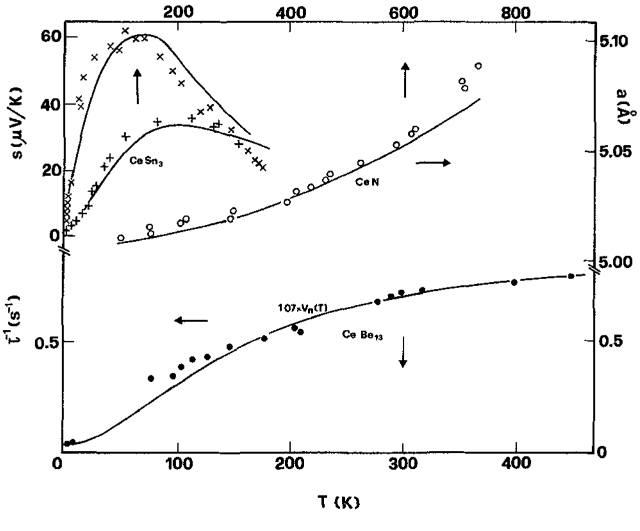

Fig. 1. — Experimental data and theoretical fitting curve of the temperature dependence of : $CeBe_{13}$ (×) and $CeSn_3$ (+) thermoelectrical power (upper right scale), CeN (○) lattice parameter (upper left scale) and $CeBe_{13}$ (●) nuclear spin-lattice relaxation rate (lower scale).

spin-lattice relaxation rate of $CeBe_{13}$ [6] and the *lattice parameter* of CeN[7] as a function of temperature are compared with the experimental data in figure 1.

As it is well known there exists a strong dependence of the Ce atomic volume from the valence. To confirm the fact that all possible behaviours of Ce in intermetallic compounds can be described from its two lower energy configurations, we have plotted in figure 2 the Ce ionic radius (r_i) [3] *vs.* E_{ex} of the compounds where $E_{ex} < E'$. It is remarkable that the compounds whose structures are : $AuCu_3$, Pu_2C_3, NaCl, $NaZn_{13}$ and CaB_6 are practically on the same line. The departure from this general behaviour of the Laves phases ($MgCu_2 \equiv AB_2$) can be understood taking into account the extra compression supported by the element A to obtain the ratio $r_A/r_B \simeq 1.33$, which characterises these phases.

A more general expression of $V(T)$ is actually studied using the Fermi distribution for $f_n(E)$ and a Lorentzian function for $D_n(E)$ in view of having a better fit also in the case of $E_n \ll T$.

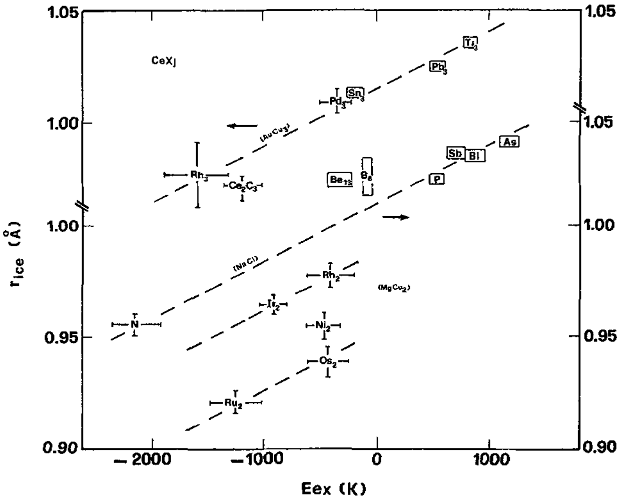

Fig. 2. — Ce ionic radius (r_{iCe}) *versus* the interconfigurational excitation energy (E_{ex}) of the compounds having $E_{ex} < E'$. Only the Ce partner is marked (except in the case of Ce_2C_3).

References

[1] Hirst, L. L., *Phys. Kondens. Mater.* **11** (1970) 255.
[2] Sales, B. C., *J. Low Temp. Physics* **28** (1977) 107.
[3] Olcese, G. L. and Sereni, J. G., To be published.
[4] Wohlleben, D., *J. Physique Colloq.* **37** (1976) C4-231.
[5] Cooper, J., Rizzuto, C. and Olcese, G. L., *J. Physique Colloq.* **32** (1971) C1-1136.
[6] Borsa, F. and Olcese, G. L., *Phys. Status Solidi* (a) **17** (1973) 631.
[7] Olcese, G. L., To be published.