Low temperature specific heat of rocksalt thorium compounds

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Résumé. — Des mesures de chaleur spécifique de $ThC_{0,75}$, $ThC_{0,6}N_{0,4}$ et ThP ont été effectuées entre 2 et 15 K. On en a déduit la valeur de la température de Debye θ_D et de la densité d'états au niveau de Fermi N_F de ces trois composés. N_F croît avec la concentration en lacunes dans ThC_{1-x} et est minimale pour $ThC_{0,6}N_{0,4}$ par rapport à ThC et ThN.

Abstract. — The specific heat of $ThC_{0,75}$, $ThC_{0.6}N_{0.4}$ and ThP samples has been measured in the range 2-15 K. From the results, the Debye temperature θ_D and the density of states at the Fermi level N_F of the three compounds have been calculated. N_F increases with vacancy content in ThC_{1-x} and is minimal for $ThC_{0.6}N_{0.4}$ compared to ThC and ThN.

1. **Introduction.** — Thorium reacts with carbon and nitrogen to form face centred cubic ThC and ThN ; ThC is stable over a large range of composition. Moreover, ThC and ThN are mutually soluble and can form ThC_xN_{1-x} compounds. The electronic structure of these compounds and others as ThP is still not well known [10]. By making specific heat measurements at low temperature, the density of states at the Fermi level has been evaluated for $ThC_{0.75}$, $ThC_{0.6}N_{0.4}$ and ThP ; further, its stoichiometry and VEC (Valence Electron Concentration) dependence has been interpreted.

2. **Experimental.** — The specific heat of $ThC_{0.75}$, $ThC_{0.6}N_{0.4}$ and ThP samples has been measured in the range 2-15 K, using an adiabatic calorimeter [1]. The samples were prepared by the classical process of reaction-sintering. Their lattice parameters (called a) are given in table I.

3. **Results.** — At low temperature, the specific heat C can generally be interpreted in terms of $C = \gamma T + \alpha T^3$, where γ is proportional to the electronic density of states at the Fermi level N_F, and α is proportional to $1/\theta_D^3$, θ_D being the Debye temperature linked with the acoustic modes of the lattice vibrations. Figure 1 shows the observed variation of C/T *versus* T^2 in the range 2-10 K for $ThC_{0.75}$; by a linear fit of the experimental data below 7 K, we

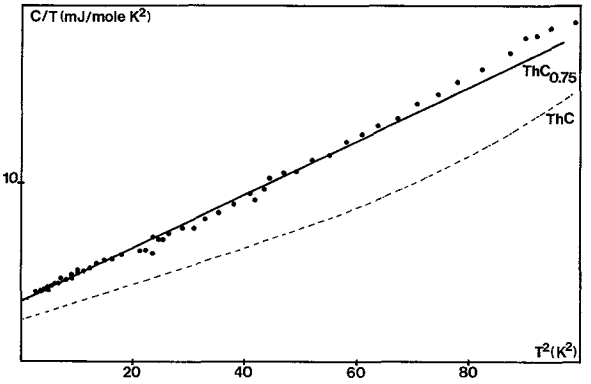

Fig. 1. — Low temperature specific heat of $ThC_{0,75}$: C/T *versus* T^2 (•: experimental data ; — : linear fit ; - - : J. Danan's experimental curve for ThC [2]).

Table I.

	$ThC_{0.75}$	ThC [2]	$ThC_{0.6}N_{0.4}$	ThN [3]	ThP
γ (mJ/mole.K²)	3.38	2.12	1.9	3.12	2.86
N_F (st/eV . at. Th)	1.43	0.9	0.81	1.32	1.21
θ_D (K)	238	262	262	284	214
a (Å)	5.32	5.34	5.27	5.16	5.84
10^4 K-^{13}C [8]	7.8	7.6	6		4.4-^{31}P
10^4 K-^{15}N [8]			8.5	8.8	
TT_1 (s.K)-^{13}C [8]	67	74	104		16.2-^{31}P
TT_1 (s.K)-^{15}N [8]			1 047	785	

have calculated the values of γ and α, and deduced θ_D and N_F. The experimental data obtained for $ThC_{0.6}N_{0.4}$ and ThP have been treated in the same way (1) ; all the results are given in table I, where they are compared to published literature values for similar compounds of other compositions. Besides, on figure 2 we can see that $ThC_{0.6}N_{0.4}$ is a superconductor. The *bump* observed in the experimental curve is not as sharp as a theoretical one ; this might be due to a slight inhomogeneity of the sample. Resistivity measurements (Fig. 2) show that at $T_2 = 4.2$ K, only a portion of the sample becomes superconducting ; the transition for the whole sample occurs at $T_1 = 3.8$ K, temperature at which it becomes diamagnetic, as we checked by magnetic susceptibility measurements. Moodenbaugh *et al.* have found ThP to be a superconductor [4] ; the transition temperature $T_c = 0.2$ K is too low to be observed in our specific heat measurements.

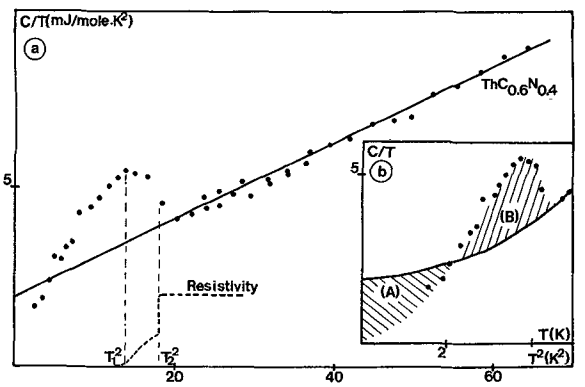

Fig. 2. — Low temperature specific heat and resistivity of $ThC_{0.6}N_{0.4}$. (a) : C/T *versus* T^2 ; (b) : C/T *versus* T.

4. **Discussion.** — There are five points that we want to discuss in the present section :

4.1 First, we observed an increase of the density of states at the Fermi level with increasing vacancy content in ThC_{1-x}, in agreement with Satow's [5] and Aronson's [6] magnetic susceptibility measurements. The fact that the ^{13}C Knight shift K and the spin-lattice relaxation rate T_1 do not vary from ThC to $ThC_{0.75}$ (see Table I) shows that the electronic structure of carbon is practically unmodified by non-stoichiometry ; the increase of N_F is then attributed to thorium 6d states.

4.2 Furthermore, N_F is minimal for $ThC_{0.6}N_{0.4}$, compared to ThC and ThN. The same conclusion had been obtained from previous ^{13}C and ^{15}N MNR experiments [7, 8] (minimum of K and maximum of TT_1 for the composition $ThC_{0.6}N_{0.4}$). This minimum is not observed for the magnetic susceptibility which increases continuously with increasing VEC for thorium carbonitrides [6]. From our results, using a rigid band model, $ThC_{0.6}N_{0.4}$ would correspond to the VEC value for which the 2p-6d bonding band is filled up.

4.3 In addition to this, $ThC_{0.6}N_{0.4}$ being a superconductor, the enhancement of γ due to the electron-phonon interaction can be evaluated ; using the McMillan equation [9] with $T_c = 3.8$ K, and taking 0.13 for the electron-electron coupling constant as it is commonly done for transition metals and alloys, we obtained the *bare* density of states at the Fermi level ; its value is

$$N_F^* = 0.59 \text{ states/eV/at. Th}$$

instead of 0.81 as it is shown in table I.

4.4 ThP and ThN, which are isoelectronic, have very close γ values and therefore very similar electronic properties.

4.5 The measured densities of states at the Fermi level for stoichiometric ThC, ThN and ThP are in qualitative agreement with those calculated by Imoto *et al.* [10] by the tight-binding method.

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(1) In the case of superconducting $ThC_{0.6}N_{0.4}$, on a C/T *versus* T diagram (Fig. 2*b*), the areas (A) and (B) on each side of the $\gamma + \alpha T^2$ curve were found equal as predicted theoretically : at the transition, the entropy remains a continuous function of T.

References

[1] ABBE, D., Thesis (1976), University of Paris-Jussieu.
[2] DANAN, J., *J. Nucl. Mater.* **57** (1975) 280.
[3] DE NOVION, C.-H., COSTA, P., *J. Physique* **33** (1972) 257.
[4] MOODENBAUGH, A. R., JOHNSTON, D. C., VISWANATHAN, R., *Bull. Am. Soc.* **22** (1977) 52.
[5] SATOW, T., *J. Nucl. Mater.* **21** (1967) 343.
[6] ARONSON, S., AUSKERN, A. B., *J. Chem. Phys.* **48** (1968) 1760.
[7] BOUTARD, J. L., DE NOVION, C.-H., *Plutonium 1975 and other actinides* (North Holland publishing Company) 1976, p. 505.
[8] BOUTARD, J. L., thesis (1976) University Paris-Sud Orsay, Report CEA-R-4797 (1976).
[9] MACMILLAN, W. L., *Phys. Rev.* **167** (1968) 331.
[10] IMOTO, S., ADACHI, H., HORI, T., *J. Nucl. Sci. Technol.* **12** (1975) 711.