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X-ray absorption and Mössbauer study of the CeSb–CeTe system

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Abstract

CeSb is a cubic trivalent Ce compound. Its very abnormal magnetic diagram contains 16 different phases depending on magnetic field and temperature. These complex physical properties could be interpreted in the framework of the p–f mixing model based on a strong mixing interaction between 4f electrons and p-band holes. The substitution of Sb by the less electronegative element Te, filling the p-valence band, modifies the hole concentration and yields very important effects. Thus, the study of the Ce(Te)Sb system is a good tool to check the validity of the model.

In this paper we present a study of the CeSb$_{1-x}$Te$_x$ solid solution by X-ray absorption experiments at the Ce and Sb L$_{III}$ edge and by Mössbauer spectroscopy (^{121}Sb, ^{125}Te). From these results, the evolution of the nature of the chemical bonding under substitution is discussed, in correlation with the x-dependence of the electronic and magnetic properties.

Keywords: CeSb$_{1-x}$Te$_x$; X-ray absorption; Sb and Te Mössbauer spectroscopy

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1. Introduction

CeSb is a compound of the trivalent cerium Ce^{3+} crystallising in the NaCl-type cubic structure. The $^2F_{5/2}$ multiplet of the Ce^{3+} ion is split, by the cubic crystal field, into a doublet Γ_7 and a quadruplet Γ_8 separated by the crystal-field energy Δ_{CF}. The physical properties of this compound are very unusual:

- the crystal-field energy Δ_{CF} is very small and the same order as the magnetic interaction;
- the magnetic anisotropy along the cube-edge directions of the NaCl lattice is very large;
- its magnetic phase diagram is very complicated: 16 antiferromagnetic phases can be distinguished in the magnetically ordered range depending on temperature and magnetic field. All these magnetic phases can be described as a stacking of up and down ferromagnetic and non-magnetic (100) planes [1].

This original behaviour of CeSb is due to the existence of strong and anisotropic interactions between the Ce^{3+} ions. Two different interpretations of the origin of these interactions have been given. Kasuya's group has developed the so-called p–f mixing, based on the semi-metallic character of CeSb [2–4], deduced from band structure calculations. In this model the coupling between the magnetic ions is mediated by the holes existing in the valence band. The second interpretation developed by Cooper's group studied the consequences of an anisotropic indirect interaction, as previously derived by Coqblin and Schrieffer, using a Schrieffer–Wolf transformation [5].

In CeSb, the substitution of Sb by Te corresponds, at least in the small Te concentration range, to the addition of conduction electrons and, so, in the hypothesis of the p–f mixing model, to the filling of the valence band. Thus, the study of the CeSb$_{1-x}$Te$_x$ solid solution provides a way to check the models by continuously varying the p-hole concentration.

Previous studies [6] of the magnetic and electrical properties of the CeSb$_{1-x}$Te$_x$ solid solution show that it exists for all values of x ($0 \leq x \leq 1$), retains the c.f.c. structure and orders antiferromagnetically at low tem-

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perature. At very low Te concentration, T_N drops very abruptly from 16 K to 4 K, the strong anisotropy disappears and the crystal electric field increases. The magnetic behaviour simplifies and becomes antiferromagnetic of type I, for $x = 0.05$. At higher Te concentration Δ_{CF} passes through an extremum. An anomalous thermal variation of the magnetic susceptibility is evidenced which can be an indication of a change in the sign of Δ_{CF}. In this case Γ_8 would become the ground state at a critical Te concentration. These results evidence the influence of the p-hole and free carrier concentration on the physical properties of CeSb. The determination of a critical concentration of Te around 3–5% for the disappearance of the anomalous properties described above seems to be in agreement with the band structure determination in CeSb. Obviously this variation in the free carriers concentration must induce a variation in the nature of the chemical bonding. In correlation with the evolution of the physical properties with composition, we present here a study of the nature of the chemical bonding in the $CeSb_{1-x}Te_x$ solid solution by means of Ce and Sb L_{III} absorption edge measurements and ^{121}Sb and ^{125}Te Mössbauer spectroscopy.

2. Experimental

Single crystals of the solid solution were obtained by direct reaction between the elements in arc welded molybdenum crucibles under argon atmosphere during a slow cooling from 2000°C. Characterisation including metallographic observation, electron microprobe analysis, X-ray diffraction experiments, magnetic susceptibility and transport measurements, were previously described [6].

The ^{125}Te Mössbauer measurements were performed at the IKS in Leuven with a conventional constant acceleration spectrometer. The γ source used was $Mg_3^{125m}TeO_6$ obtained by the irradiation of $Mg_3^{124}TeO_6$ [7].

The ^{121}Sb Mössbauer experiments were performed at LPMS in Montpellier using a ^{121m}Sn in $CaSnO_3$ source of nominal activity 0.5 mCi.

Throughout this paper, in the case of ^{121}Sb and ^{125}Te, δ is the isomer shift, Δ the Mössbauer quadrupolar splitting and Γ the half maximum full line width.

The absorbers were prepared from single crystals ground and sifted to 60 μm and mixed with A-Piezon grease to protect the powder from air. The masses of the samples correspond to ^{125}Te (natural abundance 6.99%) or ^{121}Sb (natural abundance 57.25%) of roughly 1 mg cm^{-2} and 5 mg cm^{-2} respectively.

During the measurements, both source and absorbers were simultaneously cooled at liquid helium temperature. At this temperature the Mössbauer effect is maximal (large recoil free fraction). It decreases with temperature. The refined half maximum full widths are characteristic of Sb and lead to an accurate determination of the isomer shift.

The velocity scale was calibrated from the standard spectrum of an iron absorber obtained by using a ^{57}Co source. The zero velocity was defined from the spectrum of Mg_3TeO_6 at 4 K ($\delta = 0$, $\Delta = 0$ and $\Gamma = 7.27(4)$ mm s^{-1}) for ^{125}Te and InSb at 80 K ($\delta = 0$, $\Delta = 0$ and $\Gamma = 1.79(6)$ mm s^{-1} with $\delta = -8.79$ mm s^{-1} relative to the $CaSnO_3$ source) for ^{121}Sb.

The data were analysed by adjusting experimental and theoretical spectra [8]. The quality of the refinements of the different Mössbauer parameters was checked by the usual χ^2 and 'misfit' statistical test [9]. Details about the ^{125}Te Mössbauer spectroscopy of rare-earth monotellurides solid solutions have been previously published [10].

X-ray absorption spectroscopy (XAS) measurements were done at the LURE (Orsay), on the XAS3 line, at room temperature. Pure Cu sample was used for calibration. The monochromator was a (111) Si single crystal. Samples consisted of 60 μm powder enclosed by Kapton under argon atmosphere to avoid air contamination.

3. Results

3.1. Mössbauer spectroscopy

Mössbauer spectroscopy allows the characterisation of the local electronic structure. The isomer shift δ measures the s density at the nucleus, the quadrupolar interaction Δ gives information about the local environment and the half maximum full line width Γ informs on the chemical ordering and the site distribution in the material.

For all compositions of the $CeSb_{1-x}Te_x$ solid solution studied, the ^{121}Sb and ^{125}Te Mössbauer spectra are single line ($\Delta = 0$) (Table 1 and Figs. 1 and 2).

The Sb isomer shift in CeSb is very close to its value in InSb and it increases with x. An x^2-dependence can be inferred (Fig. 3): $\delta = -1.118x^2 + 1.445x + 0.0332$.

The ^{125}Te isomer shift (determined with respect to Mg_3TeO_6) decreases between 1.14 and 1.05 mm s^{-1} when the Te concentration increases. As deduced from the scale of the ^{125}Te isomeric shift previously published [10], these values are characteristic of the divalent ionic tellurium Te^{2-}.

The isomer shift δ is given by:

$$\delta = \left(\frac{4\pi}{5}\right) Ze^2 S(Z) R^2 \frac{\Delta R}{R} \left(|\Psi_0|^2_{ab} - |\Psi_0|^2_{s}\right)$$

Table 1
^{121}Sb and ^{125}Te Mössbauer data for the $CeSb_{1-x}Te_x$ solid solution

	^{121}Sb			^{125}Te		
	δ^a ($mm\ s^{-1}$)	Δ ($mm\ s^{-1}$)	Γ ($mm\ s^{-1}$)	δ^b ($mm\ s^{-1}$)	Δ ($mm\ s^{-1}$)	Γ ($mm\ s^{-1}$)
CeSb	0.03(3)	+11.9(5)	2.1(1)	—	—	—
$CeSb_{0.9}Te_{0.1}$	0.17(1)	0	1.91(2)	—	—	—
$CeSb_{0.7}Te_{0.3}$	0.37(1)	0	1.45(2)	1.14(5)	0	5.9(2)
$CeSb_{0.5}Te_{0.5}$	0.47(1)	0	1.324(8)	1.12(4)	0	5.8(1)
$CeSb_{0.3}Te_{0.7}$	0.50(2)	0	1.12(5)	—	—	—
CeTe	—	—	—	1.05(3)	0	6.0(1)

[a] Relative to InSb at 80 K.
[b] Relative to Mg_3TeO_6 at 4.2 K.

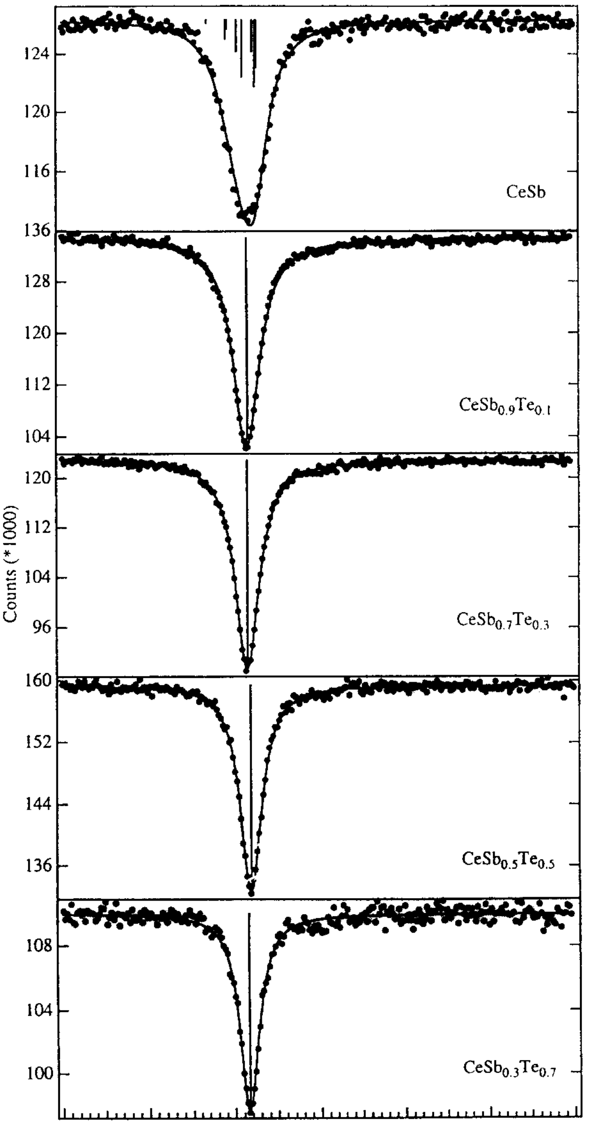

Fig. 1. ^{121}Sb Mössbauer spectra at 4.2 K for some samples of the Ce(Te)Sb solid solution.

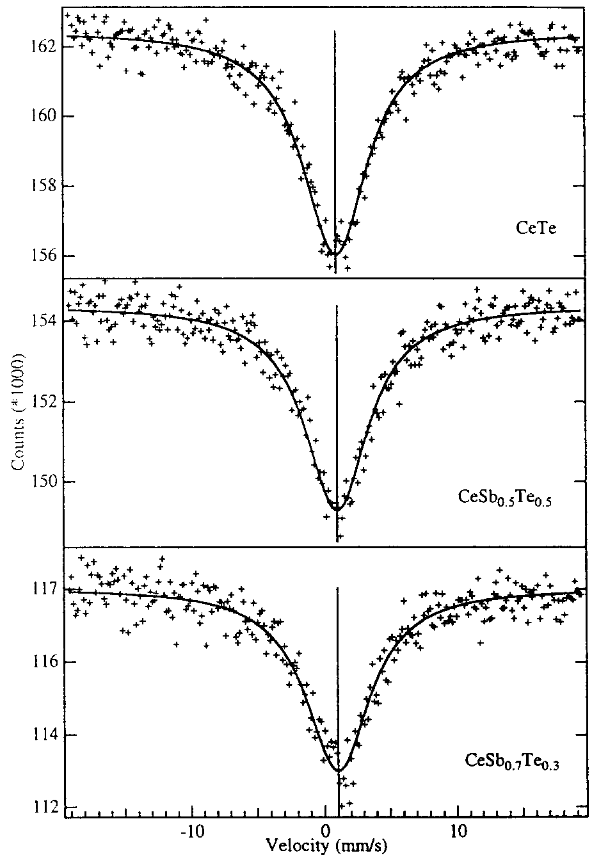

Fig. 2. ^{125}Te Mössbauer spectra at 4.2 K for some Ce(Te)Sb solid solution samples.

where R is the radius in the fundamental state, $|\Psi_0|^2$ is the electronic density at the nucleus, ab signifies absorber, s is the source, e is the electron charge, Z is the atomic number, $S(Z)$ is a relativistic correction factor, and $\Delta R/R$ is the variation of the nuclear radius between the ground state and the excited state. Since $\Delta R/R$ is negative for Sb and positive for Te, the x-dependence of the ^{121}Sb and ^{125}Te isomer shift both reflect a decrease of the s electron concentration and/or a variation of the covalency of the bond. Mössbauer spectroscopy measurements for concentrations lower than 10% are then needed to evidence the expected difference in the behaviour at large and small concentrations.

In CeSb, the large value of the half maximum full line width ($\Gamma = 2.10$ mm s^{-1} with a quadrupolar

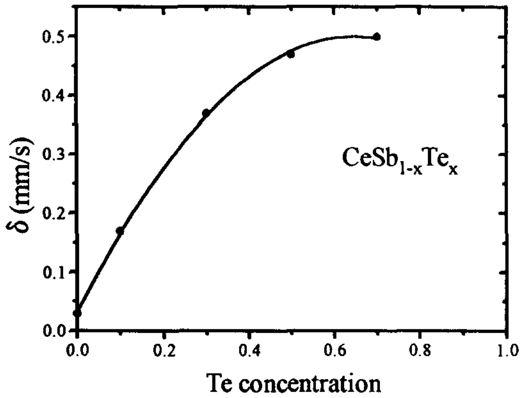

Fig. 3. x-dependence of the ^{121}Sb isomer shift. The full line is the result of the x^2 refinement (see text).

splitting equal to 11.9 mm s^{-1}), compared with InSb, evidences the existence of a transferred hyperfine field on the Sb nucleus in good agreement with the results of Holbourn and Woodhams [11]. It increases when the temperature decreases (Fig. 4) due to the appearance of a magnetic ordering at low temperature. We did not try to detect possible anomalies in the thermal variation of Γ correlated to the different magnetic transitions. The variation of Γ with x clearly reveals the abnormal behaviour of $CeSb_{0.90}Te_{0.10}$ ($\Gamma = 1.91$ mm s^{-1} with $\Delta = 0$) with respect to the other studied compositions (Fig.5). It is worth noting that this x-dependence of Γ cannot be due to the influence of the magnetic ordering as, at 4.2 K, only CeSb is magnetically ordered ($T_N = 3.10$ K for $x = 0.10$). So it is the Γ value for $x = 0$ that is overestimated which reinforces the abnormal character of $CeSb_{0.9}Te_{0.1}$.

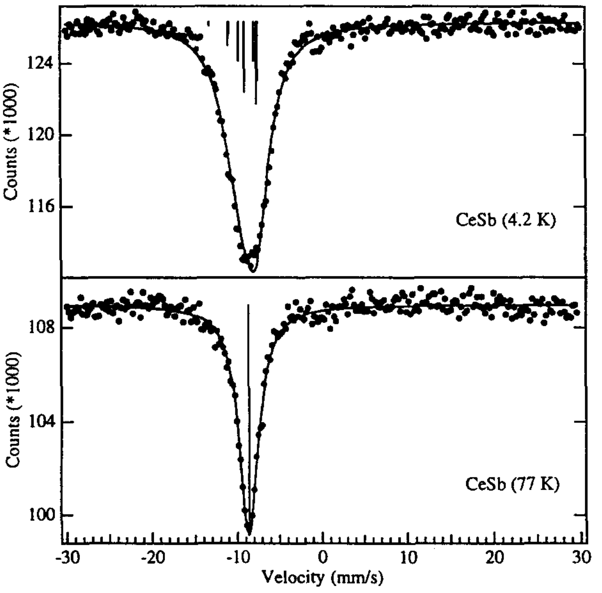

Fig. 4. Enhancement of the ^{121}Sb half maximum full line width in CeSb as the temperature is decreased, evidencing the existence of a transferred hyperfine field on the Sb nucleus.

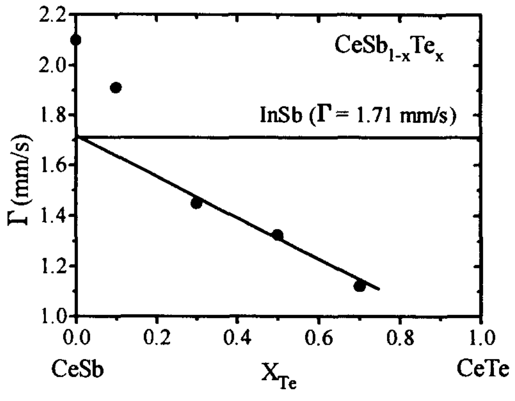

Fig. 5. x-dependence of the half maximum full line width of the ^{121}Sb Mössbauer spectra.

3.2. X-ray absorption measurements

The X-ray absorption measurements (XAS), by means of the determination of the absorption edge, allow the characterisation of the first empty levels in the conduction band. The transition energies are correlated with the effective charge of the absorbing ion, the site symmetry, the chemical nature of the neighbourhood and to the nature of the chemical bonding. The after edge structures (X-ray absorption near edge structure—XANES) give information about the local environment of the resonating atom (first and second neighbour distances, for example).

The XAS measurements at the L_{III} Ce edge (5724 eV) show a white line (Fig.6), characteristic of the trivalent cerium (Ce^{3+}) in agreement with the magnetic susceptibility measurements.

The XANES varies with composition (Fig.7). It contains only one maximum in the case of CeSb

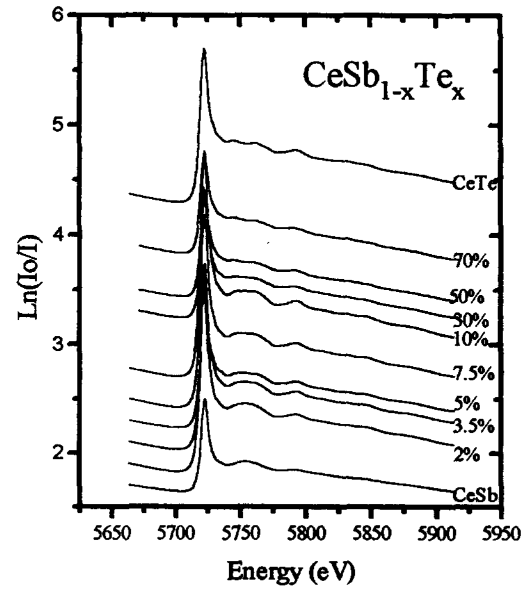

Fig. 6. Evolution of the Ce^{3+} L_{III} edge in the $CeSb_{1-x}Te_x$ solid solution with x.

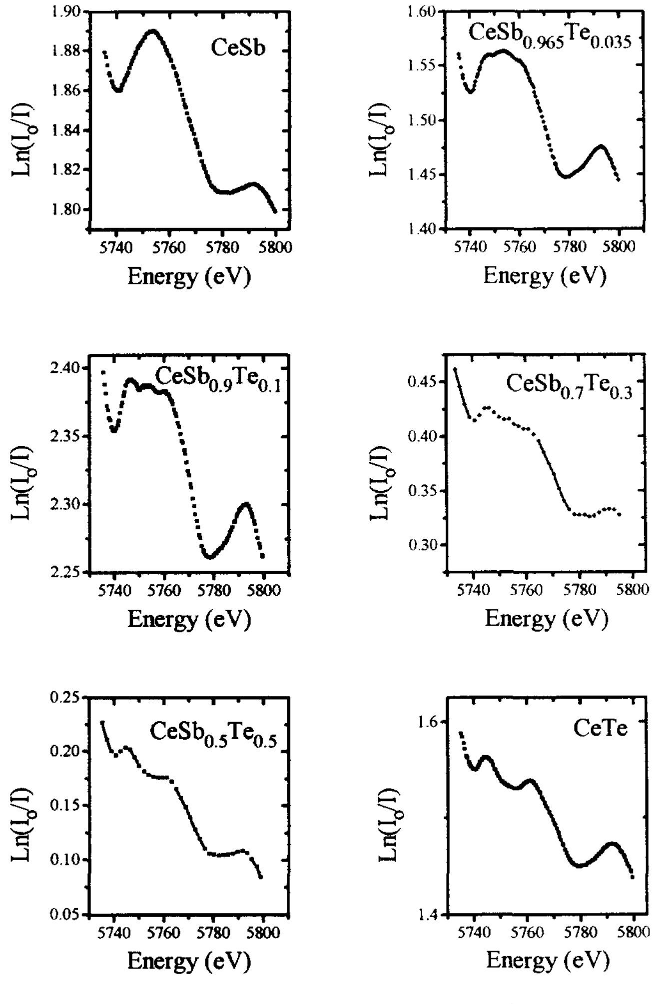

Fig. 7. Evolution of the XANES structure of the Ce^{3+} L_{III} edge in the $CeSb_{1-x}Te_x$ solid solution with the composition.

($E = 5753$ eV) and two maxima for CeTe ($E = 5745$ and 5761 eV) symmetric with respect to the maximum for CeSb. Only 2% Te is enough to generate the two maxima observed in CeTe. The area delimited by the XANES curve and the two energies relative to CeTe is strongly dependent on x for the small rate of substitution ($x \leq 0.10$) then varies slowly with x.

Unlike the L_{III} Ce edges, the Sb L_{III} absorption edges do not show a sharp white line structure but show a jump in the absorption at the edge energy. However, a weak structure can be seen on the rising edge which results from a transition from the inner p state to the empty s and d symmetry states in the conduction band [12]. The simulation of the experimental spectra takes into account the step function at the absorption energy and the Lorentzian and Gaussian broadening due respectively to the life-time of the initial state and the instrumental resolution. Using this procedure, previously described [13], we can extract the s and d contributions which can be assimilated to two Gaussians (Fig. 8). The lowest peak at the Sb L_{III} edge was attributed to 5s (Sb) states, the highest one being due to the 5d states. Since all absorption curves are normalized to the same absorption height, the areas measured under the s-structure may be compared for the different $CeSb_{1-x}Te_x$ compositions. The x-dependence of the area of the lower energy contribution (2p–5sσ^*) is presented in Fig.9. The variation of the Sb Mössbauer half maximum full line width clearly shows an anomaly around $x = 0.10$.

4. Discussion and conclusion

Our Mössbauer spectroscopy and X-ray absorption studies of the $CeSb_{1-x}Te_x$ solid solution confirm the abnormal character of $CeSb_{0.9}Te_{0.1}$. The x-dependence of the ^{121}Sb half maximum full line width shows that this compound is the boundary between two domains with different physical properties. This interpretation is in agreement with the band structure calculations [2–4], magnetic measurements and neutron diffraction experiments [1], from which the existence of holes in the valence band of CeSb is inferred.

In CeSb, the valence band is built with the p state of the pnictogene and the conduction band with the s and d states of the cerium. As the isomer shift is directly sensitive to the s density at the nucleus, it is very surprising that no anomaly could be detected in the δ variation at the critical concentration. More ^{121}Sb Mössbauer spectroscopy measurements are needed at low concentrations ($x < 0.10$).

The half maximum full line width is an indicator of the distortion of the site due to the substitution. This distortion is firstly linked to the difference in the electronegativity between Sb and Te. Our results indicate that the difference is a maximum at a Te concentration close to the filling of the valence band.

The intensity of the 2p–5sσ^* is a maximum around $x = 0.10$. This intensity is correlated to the occupancy of the p Sb, Te states and to the density of the empty s and d Ce^{3+} states in the conduction band. The increase observed at low Te-concentration ($x \leq 0.10$) could be correlated to the filling of the valence band which increases the density of electrons able to absorb the photon energy. For $x > 0.10$, no more holes exist in the valence band and the decrease of the intensity of the transition could be correlated to the filling of the lower s and d states in the conduction band.

In conclusion, we have studied the $CeSb_{1-x}Te_x$ solid solution by means of ^{121}Sb and ^{125}Te Mössbauer spectroscopy and Ce and Sb L_{III} absorption edge measurements in order to correlate the evolution of the nature of the chemical bonding under the modifications of the free carrier concentration with the

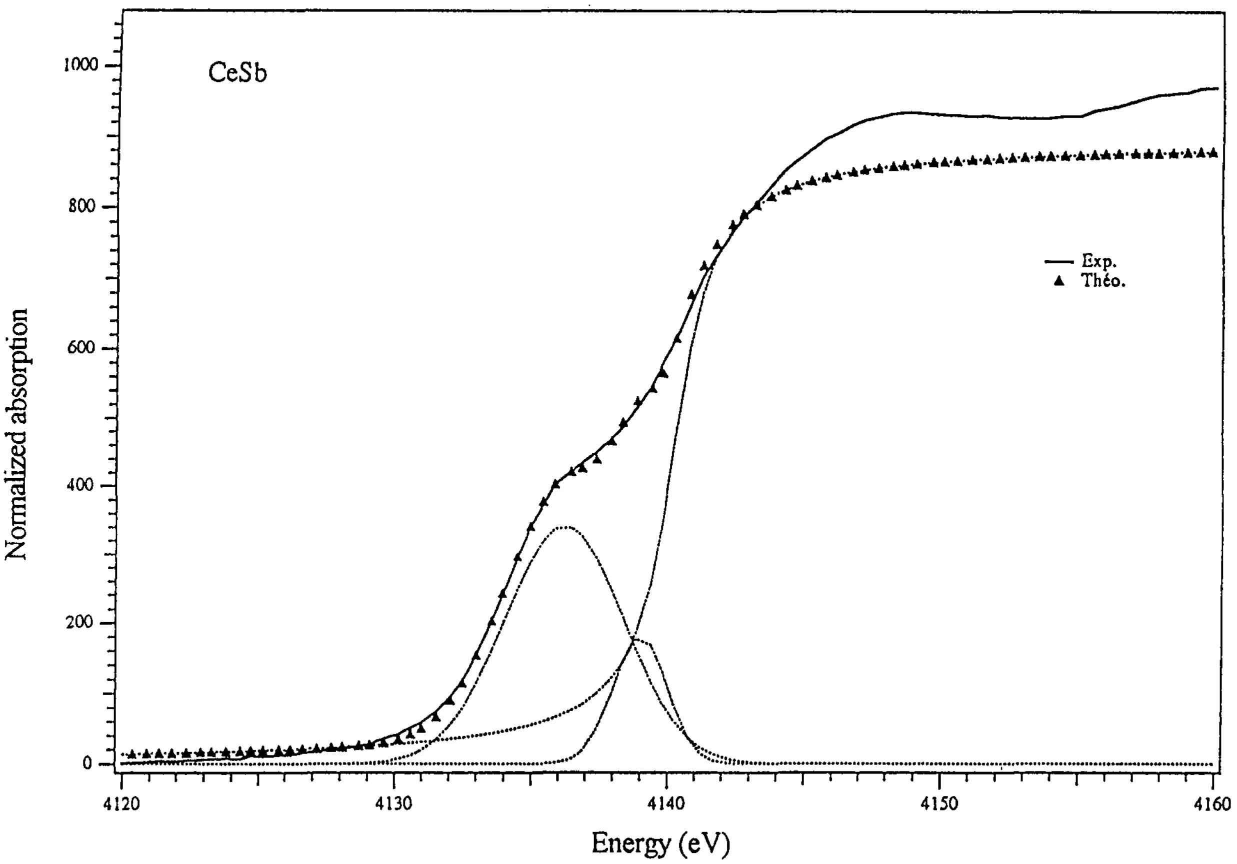

Fig. 8. Sb L_{III} edge in CeSb and its deconvolution.

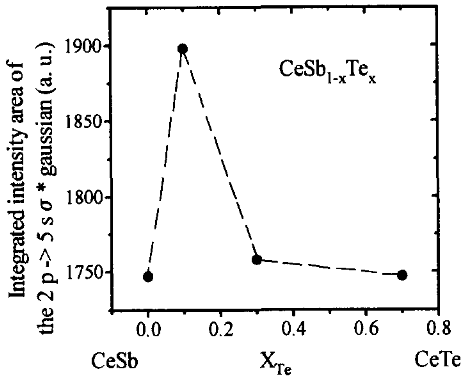

Fig. 9. Variations of the measured areas under the s structure at the L_{III} edge of Sb as a function of x.

physical properties. We show that the abrupt change in the magnetic properties for x lower than 5% can be associated to an anomaly in the x-dependence of the ^{121}Sb Mössbauer half maximum full line width and the integrated intensity of the area under the s structure at the L_{III} edge of Sb. This behaviour is attributed to the existence of holes in the valence band for which the progressive disappearance under substitution is responsible for the modification of the physical properties and of the chemical bonding.

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