

Electronic configuration of cerium in amorphous alloys investigated by x-ray absorption spectroscopy

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X-ray absorption-edge measurements were used to investigate the electronic configuration of cerium in different series of amorphous alloys, namely the Ce-Si alloys and the intermetallic Ce-Ni and Ce-Co alloys. The effect of structural disorder is evaluated from a comparison of our data on amorphous alloys with those obtained for compositionally related crystalline compounds. While the L_{III} absorption edge for $CeSi_2$ exhibits a weak valence anomaly, the trivalent configuration of cerium is stabilized by the topological disorder in amorphous alloys over the whole concentration range we investigated ($0.10 \leq x \leq 0.80$). In contrast, strong valence anomalies on cerium are retained in amorphous Ce-Ni and Ce-Co alloys without any significant effect attributable to amorphicity.

I. INTRODUCTION

Among the so-called "mixed-valence" systems, the cerium-based compounds or alloys have been investigated very extensively in the last decade.¹⁻³ Unusual physical properties observed in homogeneous mixed-valent systems are commonly explained by charge fluctuations between two nearly degenerate electronic configurations differing by the $4f$ occupation number (closely related to the valence). In the past five years, an intensive effort has been devoted to determining the valence of cerium. High-energy photon and electron emission and absorption techniques, involving characteristic times very short with respect to charge fluctuations, have proved very reliable in measuring the nonintegral Ce valence^{4,5} in its ground state.

As illustrated by the phase diagram for pure cerium metal, the valence of cerium is very sensitive to thermodynamical parameters such as pressure and temperature. This is also well established for many Ce-based compounds and alloys. In contrast, the influence of structural parameters such as neighboring vacancies or interstitials, impurities or lattice defects, nonstoichiometry, etc., on the Ce valence is less documented. If such effects have been observed in several crystalline Ce-based compounds, systematic studies along this line have remained scarce to date.¹ Amorphous alloys containing Ce ions might provide a broad variety of new systems where the stability of the mixed valence state with respect to structural disorder can be probed.

It has already been shown that the cerium remains purely trivalent in amorphous alloys such as Ce rich Ce-Cu, Ce-Al, and Ce-Au alloys,⁶ where crystalline counterparts contain cerium in a normal $4f^1$ magnetic state. We undertook an extensive study of two series of amorphous alloys, namely the Ce-Si system, where the crystalline

$CeSi_2$ compound exhibits a weak valence anomaly (α -Ce-type compound) and the intermetallic Ce-Ni and Ce-Co amorphous alloys, whose crystalline counterparts are strongly mixed valent (α' -Ce-type or "tetravalent" compounds). A preliminary report on the magnetic properties of amorphous Ce-Si alloys has already been given.⁷ We present here the results of our L_{III} x-ray-absorption (XAS) measurements on evaporated amorphous Ce-Si, Ce-Ni, and Ce-Co alloys as well as on crystalline $CeSi_2$, $CeNi_5$, and $CeCo_5$ compounds. We show that the weak valence anomaly observed in crystalline $CeSi_2$ disappears in the corresponding amorphous alloys, while the strong valence anomalies of the crystalline Ce_mCo_n and Ce_mNi_n compounds remain practically unchanged in the amorphous state, as already suggested by the magnetic, calorimetric, and transport properties of the liquid-quenched amorphous $Ce_{75}Co_{25}$ alloy.⁸ For the amorphous Ce-Ni and Ce-Co alloys, we determine the concentration dependence of the average Ce valence which indicates the role of the $3d$ band filling in the hybridization mechanism giving rise to the noninteger Ce valence.

The paper is organized as follows. Section II presents the experimental techniques. The experimental results are reported in Sec. III followed by a discussion in Sec. IV. Conclusions are given in Sec. V.

II. EXPERIMENTAL TECHNIQUES

Amorphous Ce_xSi_{1-x} , Ce_xNi_{1-x} , and Ce_xCo_{1-x} alloys were prepared by co-evaporation in an ultrahigh vacuum onto a liquid-nitrogen-cooled substrate. The preparation technique was described in detail elsewhere.⁹ The alloys were found to be amorphous by electron microscopy over the following concentration ranges: $0 \leq x \leq 0.80$ for Ce_xSi_{1-x} and $0.10 \leq x \leq 0.45$ for Ce_xNi_{1-x} and Ce_xCo_{1-x} . The samples of about $1 \mu m$ thickness were

protected from oxidation by an evaporated amorphous Si film of thickness 1000 Å.

The crystalline CeSi_2 , CeNi_5 , and CeCo_5 compounds were prepared by arc melting. Their crystal structure was checked by x-ray diffraction.

The x-ray-absorption measurements were performed by using the synchrotron radiation of the DCI storage ring at Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (LURE), Orsay. Preliminary experiments were done on an in-laboratory spectrometer using the bremsstrahlung radiation giving by a silver rotating anode working at low voltage (≤ 10 kV) in order to avoid high-order harmonics. As the L_{III} absorption edge of cerium lies in a relatively low energy range (about 5.7 keV), the thickness of the sample must not exceed a few micrometers. This requirement is easily fulfilled by piling several pieces of sample of a given concentration.

III. EXPERIMENTAL RESULTS

A. The amorphous $\text{Ce}_x\text{Si}_{1-x}$ alloys and the crystalline CeSi_2 compound

The L_{III} absorption edges of cerium in crystalline CeSi_2 and in several amorphous $\text{Ce}_x\text{Si}_{1-x}$ alloys are reported in Figs. 1(a) and 1(b). The $c\text{-CeSi}_2$ spectrum presents the two-bump structure characteristic of mixed-valent materials, the low-energy peak being attributed to the $4f^1(5d,6s)^3$ electronic configuration in the initial state, whereas the high-energy structure ($\Delta E \sim 8$ eV) is typical of the $4f^0(5d,6s)^4$ configuration. A standard fitting procedure already used and discussed by Krill *et al.*¹⁰ and others⁴ yields for $c\text{-CeSi}_2$ a $4f$ occupation number of 0.92 ± 0.02 or an average Ce valence $\bar{v} = 3.08 \pm 0.02$, in good agreement with previous L_{III} -edge measurements on the same compound ($\bar{v} = 3.05$).¹¹

In contrast, the amorphous $\text{Ce}_x\text{Si}_{1-x}$ alloys, as shown in Fig. 1(b), were found to be purely trivalent over the whole concentration range investigated ($0.10 \leq x \leq 0.80$). The weak valence anomaly in $c\text{-CeSi}_2$ does not survive the structural disorder. This stabilization of the Ce trivalent configuration in amorphous $\text{Ce}_x\text{Si}_{1-x}$ alloys is in perfect agreement with our bulk magnetization data,⁷ which showed a normal magnetic behavior in amorphous alloys down to at least 1.6 K, while $c\text{-CeSi}_2$ is nonmagnetic below a characteristic temperature of about 200 K.^{12,13}

B. The amorphous $\text{Ce}_x\text{Ni}_{1-x}$ and $\text{Ce}_x\text{Co}_{1-x}$ alloys and the related crystalline compounds

The Ce L_{III} -absorption edges in $c\text{-CeNi}_5$ and $c\text{-CeCo}_5$ are reported in Fig. 2(a). These spectra are essentially the same as those previously published by several authors^{10,14-17} showing once more that the $4f$ occupation number in these so-called tetravalent compounds is not less than 0.6. At variance with the case of amorphous Ce-Si alloys, the structural disorder does not affect in a significant way the $4f$ occupation number in amorphous Ce-Ni and Ce-Co alloys as compared with related crystalline compounds.¹⁸⁻²⁰ This point is clearly illustrated by the comparison between the spectra of Figs. 2(a) and 2(b).

Since the composition in amorphous alloys can be varied continuously, we determined the concentration dependence of the Ce valence in the amorphous $\text{Ce}_x\text{Ni}_{1-x}$ and $\text{Ce}_x\text{Co}_{1-x}$ alloys over the concentration range $0.10 \leq x \leq 0.45$. This concentration effect is demonstrated in Fig. 3 showing the Ce L_{III} spectra for amorphous Ce-Ni alloys of different compositions. When increasing the Ni content, the high-energy peak associated with the $4f^0$ occupation grows in intensity up to a saturation value of $\bar{v} = 3.33 (\pm 0.02)$. Similar concentration dependence and saturation effect are observed in amorphous Ce-Co alloys.

As shown in Fig. 4, the Ce valence saturates at about the same value $\bar{v} = 3.33$ for both series of amorphous alloys as well as for many "tetravalent" crystalline Ce compounds.¹⁸⁻²⁰ But this saturation is more easily reached (i.e., with a smaller content of transition metal) for amorphous Ce-Co than for Ce-Ni alloys.

A similar feature was already noted for crystalline Ce_mCo_n compounds compared with Ce_mNi_n compounds.²⁰ To all the above-mentioned respects, the Ce valence anomaly in these intermetallic amorphous alloys

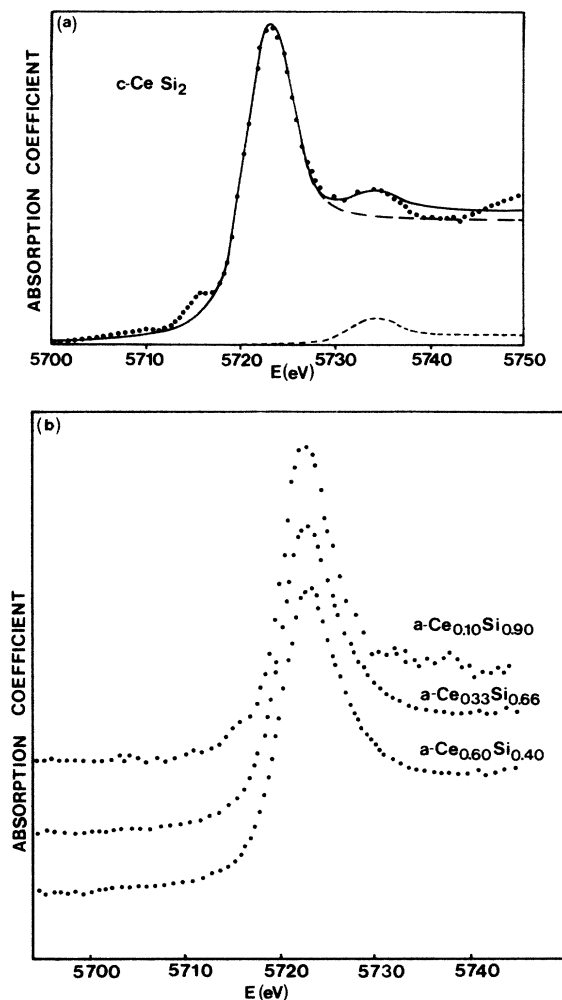


FIG. 1. Ce L_{III} -edge absorption spectra (deconvoluted from the experimental resolution) for (a) crystalline CeSi_2 and (b) several amorphous $\text{Ce}_x\text{Si}_{1-x}$ alloys.

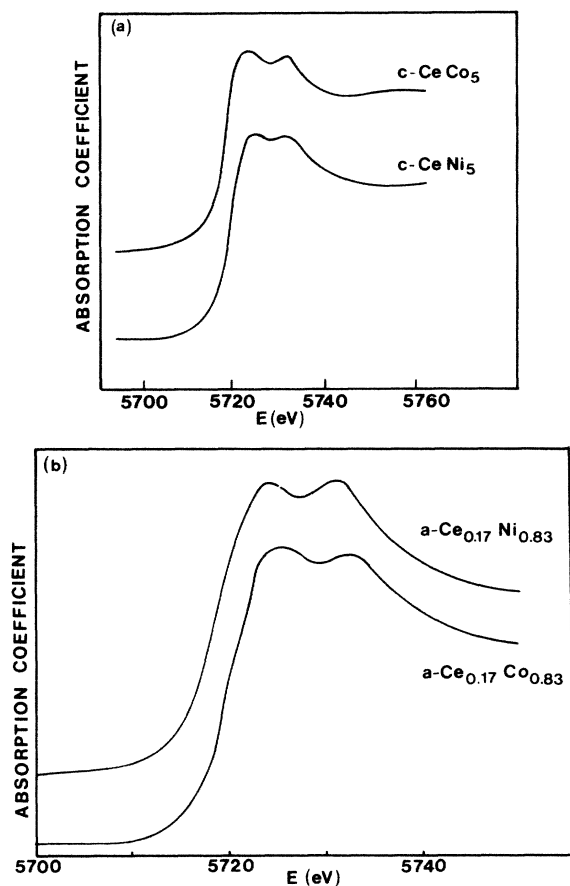


FIG. 2. Ce L_{III} -edge absorption spectra for (a) crystalline $CeNi_5$ and $CeCo_5$ compounds and (b) related amorphous alloys.

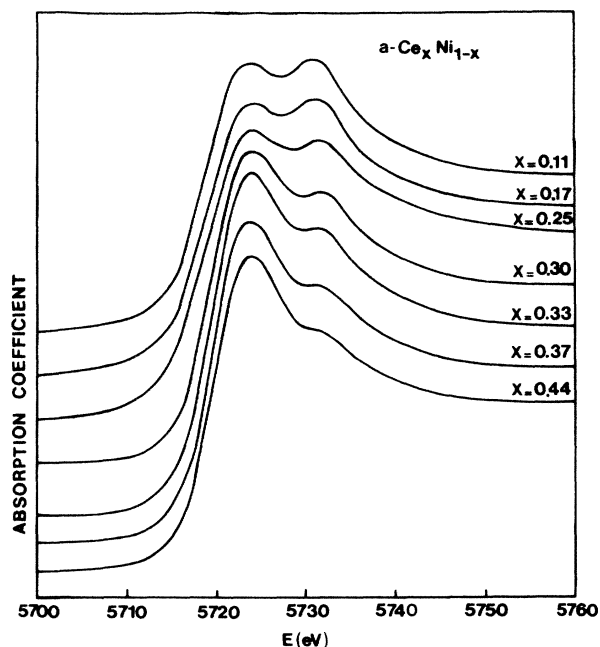


FIG. 3. Ce L_{III} -edge absorption spectra for amorphous Ce_xNi_{1-x} of different compositions.

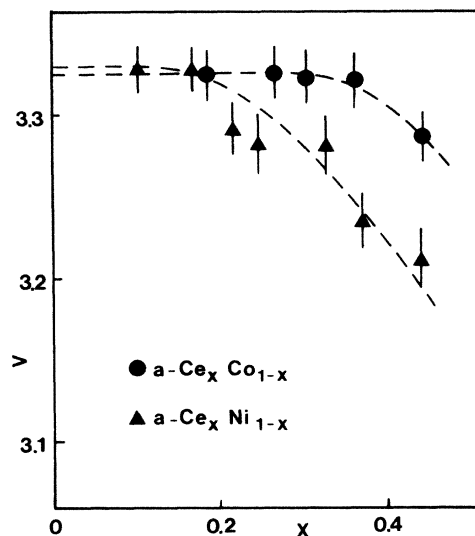


FIG. 4. Average cerium valence versus composition in amorphous Ce-Ni and Ce-Co alloys.

is not significantly affected by the structural disorder.

Preliminary x-ray photoemission-spectroscopy (XPS) measurements were also performed on these amorphous alloys and on related crystalline compounds as well. From our data and from a comparison with published XPS data on crystalline Ce_mCo_n and Ce_mNi_n compounds,^{21,22} it can be already ascertained that the $3d$ Ce core level spectra for amorphous Ce-Co and Ce-Ni alloys show evidence for a Ce valence admixture in the ground state, confirming then in a qualitative way the conclusions drawn from x-ray absorption-spectroscopy (XAS). But a quantitative analysis of our XPS spectra along with a detailed comparison with valence estimations from XAS edges would involve technical problems at several levels such as surface contamination and/or disorder, role of shake-down structures, possible underestimation by XPS of the $4f^0$ contribution in the ground state.²³ Such questions and others would be beyond the purpose of this paper and will be discussed at length elsewhere.

IV. DISCUSSION

First, we discuss the contrasted effects of structural disorder in amorphous Ce_xSi_{1-x} alloys on the one hand, and in amorphous Ce-Ni and Ce-Co alloys, on the other. Then, we comment on the saturation of the mixed valence along with the effect of d -band filling in intermetallic amorphous Ce-Ni and Ce-Co alloys as well as in their crystalline counterparts.

A. Influence of structural disorder in a Ce compound with an $s-p$ element

No trace of valence admixture was detected from either our spectroscopic measurements or our earlier magnetic data above $1.6 K^7$ in amorphous Ce_xSi_{1-x} alloys over the whole concentration range investigated. The fragile character of the mixed-valence state in crystalline $CeSi_2$ was

already demonstrated by magnetic and calorimetric measurements in off-stoichiometric compounds.¹² While *c*-CeSi₂ presents all the physical properties characteristic of a nonmagnetic ground state (namely a low Pauli paramagnetic susceptibility together with a large electronic specific heat) with a Kondo-type temperature of about 200 K, in the off-stoichiometric compounds, the “Kondo temperature” was found to decrease progressively with increasing Si deficiency until a magnetic order takes place at 10 K when the composition CeSi_{1.85} is reached. It is not clear at present whether this stoichiometry effect results from pure chemical disorder or to what extent it is related to Si vacancies. The fact that no traces of valence anomaly remain in amorphous Ce_xSi_{1-x} alloys suggests that the disorder might be predominant. It must be noted that the structural disorder in our amorphous alloys does not necessarily imply large fluctuations in the short-range order (SRO) around Ce atoms nor a drastic change in the average SRO in the amorphous alloy as compared with the SRO in the crystalline counterparts. Indeed, extended x-ray absorption fine structure (EXAFS) measurements about the Ce *L*_{III} edge showed that the interatomic distances and the coordination numbers of crystalline CeSi₂ are basically preserved in the amorphous alloy of same composition.²⁴ This result suggests that the weak mixed-valent state in *c*-CeSi₂ relies on some subtle details in the electronic band structure, which are changed as the lattice periodicity is lost. Such a significant effect of structural disorder, reported also for amorphous Ce-Al alloys,²⁵ is likely to occur in other Ce alloys with *s-p* elements, where the cerium valence anomaly is weak in the crystalline compounds.

A recent many-body calculation based on the Gunnarsson and Schönhammer model concludes that the *4f*¹ states should be located 0.25 eV below the Fermi level *E*_F in the valence band.²² In addition, a sizable *f* admixture with the *p* band is predicted by the calculation. According to that picture,²² the structural disorder in amorphous Ce-Si alloys might result in repelling *4f*¹ states further below *E*_F and/or in weakening the *p-f* hybridization and thus, stabilizing the trivalent state of cerium. It should be noted that the above-mentioned features near *E*_F in crystalline CeSi₂ coexist with a *4f*¹ peak located 2.1–2.2 eV below *E*_F, as evidenced by resonant photoemission measurements.²⁶ This bimodal nature of the *4f* states is a challenging aspect encountered in many Ce-based mixed-valent compounds.²⁷

The insensitivity to disorder in the transition metal-rich Ce compounds is in marked contrast with the case of a Ce compound with an *s-p* element such as CeSi₂. Even in the liquid state, the magnetic susceptibility of Ce-Co alloys suggests a (partial) delocalization of the Ce *4f* electron over the concentration range 38–62 at. % Ce.²⁸ It is known also that the chemical disorder on Ce in Ce diluted pseudobinary crystalline compounds has no significant influence on the Ce valence anomaly.²⁹ Similar observation was made for Yb diluted down to 1 at. % in crystalline YCuAl.³⁰ Strong valence admixture was already reported for amorphous Ce₇₅Co₂₅ (Ref. 8) and Ce₂₅Pd₇₅ alloys (Ref. 31). All these results, together with our spectroscopic data on amorphous Ce-Ni and Ce-Co alloys, suggest that

the mixed-valent state in intermetallic Ce-based systems originates in a strong *f-d* hybridization which is not affected by any degree of disorder. This point will be discussed in more detail in the following section.

B. Composition dependence of the average Ce valence in amorphous Ce-Ni and Ce-Co alloys: Saturation effect and role of the *d*-band filling

Among the most important contributions brought by x-ray-absorption spectroscopy to our knowledge of strong mixed-valent Ce compounds is the observation that a pure tetravalent state does not exist in metallic compounds and that the average Ce valence never exceeds 3.4 as determined from XAS spectra in metallic Ce compounds. This gives rise to a saturation effect in the pressure dependence of the Ce valence for elemental cerium³² or in the concentration dependence for binary Ce_mCo_n and Ce_mNi_n crystalline compounds²⁰ as well as in ternary Ce (Pd_{1-x}Rh_x)₃ (Ref. 33) or Ce (Pd_{1-x}Ag_x)₃ compounds (Ref. 34). Amorphous Ce-based alloys yield the possibility to study the change of the Ce valence in binary alloys in a continuous manner, independently of stoichiometry compositions. The most elaborated explanation of this saturation behavior and of the discrepancies between *L*_{III}-edge valence determinations and volume-derived estimations relies on thermodynamics.^{32,3,4} The free energy of elemental Ce and of Ce-based compounds is analyzed in two major terms. One is positive, almost independent of volume, and due to elastic strain. It is maximal for a valence of 3.4. The other term is negative and related to configurational mixing. The interplay of those two terms reproduces the body of available experimental data rather well. This model works in the case of strong *d-f* hybridization, but finer details in the hybridization are not taken under consideration. Therefore, small effects of structural disorder or hybridization are not likely to significantly affect this saturation behavior. Similarly, free-volume effects occurring in amorphous alloys seem to be negligible in this context.

The role of the *d*-band filling in the Ce valence admixture in intermetallic Ce-based compounds was first pointed out by spectroscopic measurements on binary Ce_mCo_n and Ce_mNi_n compounds²⁰ and in ternary Ce (Co_{1-x}Cu_x)₅ and Ce (Ni_{1-x}Cu_x)₅ compounds.³⁵ The same effect was noted for crystalline Ce (Ni_{1-x}Co_x)₂ compounds.³⁶ In the Ce compounds with Cu, no mixed-valent state occurs, but only Kondo-lattice systems, without magnetic order, such as in CeCu₆,³⁷ or with magnetic order, such as in CeCu₂.³⁸ In contrast, the mixed-valence admixture increases with transition metal content in Ce-Ni and Ce-Co alloys. This increase is steeper in Ce-Co alloys, where the saturation is reached for smaller transition-metal content than in the Ce-Ni system, as illustrated in Fig. 4. The influence of the *3d*-band filling in the Ce mixed-valent state in these intermetallic alloys can be described in different ways. In terms of charge transfer in a rigid band picture, it has been argued that the *5d* electrons are transferred to the *3d* band from electronegativity considerations, thus lowering *E*_F in the intermetallic compound as compared with *E*_F of the pure rare earth; when the *3d* band is filled up, no

transfer is possible and the Ce remains trivalent.¹⁴ The role of the *d*- or *s*-like character of the band structure in valence-fluctuating systems was evaluated in a more elaborated way for the case of Eu-based compounds.³⁹ It is known that Eu intermetallic compounds exhibit the same systematic trend as Ce-based compounds, in the sense that most of the *s*-like-band intermetallics present a normal magnetic valent state (divalent for Eu, trivalent for Ce), while mixed-valent configurations are encountered mostly in intermetallics of strong *d* character. This situation was explained by calculations within a model of a single rare-earth atom in a *d*- or *s*-like-band metal. The stability of the Eu divalent state ($4f^7$) was discussed with respect to an electron transfer to the conduction band producing a $4f^6$ configuration plus an extra conduction electron. One is then left with a one-impurity problem in which this extra electron has to be screened by the electron gas to preserve the overall charge neutrality. The screening potential is determined self-consistently to satisfy a modified Friedel sum rule. For *s*-like metals the local screening is not achieved and the normal divalent configuration is stabilized. For *d*-like metals the stability of the mixed-valent state is somewhat proportional to the filling of the *d* band, reaching a maximal value for a half-filled *d* band. A similar one-impurity model emphasizing the role of screening effects due to *d* electrons was also developed by Haldane.⁴⁰ These *d*-electron screening processes were shown to be able to induce the $4f$ charge fluctuations.

These two latter theoretical approaches lie halfway between "extreme" models for valence-fluctuation phenomena, namely the pure ionic picture on the one hand, and on the other, the one-electron band picture. Refinements to these calculations are obviously needed in order to take into account the specific aspects of the Ce problem along with the effects of rare-earth concentration and to treat in a more realistic way the electronic band structure of the intermetallic compounds. In spite of the limitations of these one-impurity calculations, the main physical effect is suggested, namely the fact that valence fluctuations in Eu- or Ce-based compounds are associated with the possibility of ensuring the local charge screening. On this basis, one could speculate that the mixed-valent state in intermetallic Ce-based alloys would be further stabilized by replacing Co by Fe while the opposite effect would be obtained with V or Ti. Some work is in progress in our group, in order to check the validity of this speculation.⁴¹

V. CONCLUSION

We showed through x-ray-absorption measurements that the weakly mixed-valent state in a Ce compound with *s-p* elements such as CeSi_2 is unstable with respect to disorder. The small Ce valence admixture which progressively decreases when increasing Ce content in off-stoichiometry crystalline compounds, was found to com-

pletely disappear in amorphous $\text{Ce}_x\text{Si}_{1-x}$ alloys for all concentrations between $x=0.10$ and 0.80 . In contrast, the strongly-mixed-valent state in Ce-Co and Ce-Ni compounds is stable with respect to structural disorder. We showed that the amorphous state in these intermetallic Ce-based alloys allows one to vary continuously the composition over rather broad concentration ranges, and then to follow the continuous increase of the average Ce valence with increasing transition-metal content up to a saturated valence state. The influence of the filling of the $3d$ band in the appearance of the mixed-valent state was evidenced and discussed in terms of screening effects within one rare-earth impurity models.

It is tempting to extend those contrasted effects to the two different families of Ce-based compounds, namely the Ce compounds with *s-p* elements (very sensitive to disorder) and the Ce compounds with *d* elements (insensitive to disorder). Further examples are clearly needed to ascertain these systematic trends for the Ce compounds and the Yb- or Eu-based metallic compounds as well. This might shed some light on mechanisms giving rise to the valence admixture in the *sp*-like compounds and in the *d*-like rare-earth intermetallic compounds, respectively.

Finally, let us make two conclusive remarks. First, the structural implications of our results on the two families of amorphous alloys we investigated are not straightforward. According to our EXAFS measurements presented elsewhere,²⁵ the average SRO does not depart much from that of the crystalline counterpart in amorphous versus crystalline CeSi_2 . On the other hand, the SRO about Co and Ni is very much the same in amorphous Ce-Co and Ce-Ni alloys, respectively, and in related crystalline compounds. But the disorder is much more pronounced around Ce in both series of amorphous intermetallic alloys. A second remark concerns the effect of structural disorder in amorphous Ce-Ni and Ce-Co alloys. While this effect is not significant as far as the Ce valence admixture is concerned, the structural disorder manifests itself on the $3d$ magnetism of these alloys, especially for the amorphous Ce-Co alloys, where the Co magnetism is substantially enhanced with respect to related crystalline compounds. This aspect will be reported in a forthcoming paper.

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¹J. M. Lawrence, P. S. Rieseborough, and R. D. Parks, Rep. Prog. Phys. **44**, 1 (1981).

²B. Coqblin, J. Magn. Magn. Mater. **29**, 1 (1982).

³D. Wohlleben and J. Röhrler, J. Appl. Phys. **55**, 1904 (1984).

⁴J. Röhrler, J. Magn. Magn. Mater. **47-48**, 175 (1985).

⁵J. C. Fuggle, Physica **130B**, 56 (1985).

⁶U. Ernst, W. Felsch, and K. Samwer, J. Magn. Magn. Mater. **15-18**, 1375 (1980), W. Felsch, S. G. Kuhsnir, and K.

- Samwer, J. Phys. (Paris) Colloq. **41**, C8-630 (1980), W. Felsch and H. Schröder, Solid State Commun. **45**, 1043 (1983).
- ⁷D. Malterre, J. Durand, and G. Marchal, J. Non-Cryst. Solids **61-62**, 1137 (1984). XAS measurements on amorphous Ce-Si, Ce-Ni, and Ce-Co alloys were already presented and discussed at the MMM Conference San Diego (Nov. 1984). J. Durand, D. Malterre, G. Marchal, G. Krill, M. F. Ravet, and J. P. Kappler, J. Appl. Phys. **57**, 3154 (1985).
- ⁸W. Felsch, S. G. Kushnir, K. Samwer, H. Schröder, R. van den Berg, and H. v. Löhneysen, Z. Phys. B **48**, 99 (1982).
- ⁹M. Piecuch, J. F. Geny, and G. Marchal, in *Amorphous Metals and NonEquilibrium Processing* (Editions de Physique, Paris, 1984), p. 79.
- ¹⁰G. Krill, J. P. Kappler, A. Meyer, L. Abadli and M. F. Ravet, in *Valence Fluctuations in Solids*, edited by L. M. Falicov, W. Hanke, and M. B. Maple (North-Holland, Amsterdam, 1981), p. 435.
- ¹¹J. M. Lawrence, M. L. den Boer, R. D. Parks, and J. L. Smith, Phys. Rev. B **29**, 568 (1984).
- ¹²H. Yashima, T. Satoh, H. Mori, D. Watabe, and T. Ohtsuka, Solid State Commun. **41**, 1 (1982); H. Yashima, H. Mori, T. Satoh, and K. Kohn, *ibid.* **43**, 193 (1982).
- ¹³W. H. Dijkman, A. C. Moleman, E. Kesseler, F. R. de Boer, and P. F. de Châtel, in *Valence Instabilities*, edited by P. Wachter and H. Boppert (North-Holland, Amsterdam, 1982), p. 515.
- ¹⁴D. Gignoux, F. Givord, R. Lemaire, H. Launois, and F. Sayetat, J. Phys. (Paris) **43**, 173 (1982).
- ¹⁵L. D. Finkel'shteyn and N. D. Sanisonova, Phys. Met. Metallogr. **53**, 4, 85 (1982).
- ¹⁶T. Mihalisin, A. HARRUS, S. Raaen, and R. D. Parks, J. Appl. Phys. **55**, 1966 (1984).
- ¹⁷M. Croft, R. Neifeld, C. U. Segre, S. Raaen, and R. D. Parks, Phys. Rev. B **30**, 4164 (1984).
- ¹⁸E. Beaurepaire, G. Krill, J. P. Kappler, and J. Röhler, Solid State Commun. **49**, 1 (1984).
- ¹⁹R. D. Parks, S. Raaen, M. L. den Boer, V. Murgai, and T. Mihalisin, Phys. Rev. B **28**, 3556 (1983).
- ²⁰A. E. Sovestnov, V. A. Shaburova, I. A. Markova, E. M. Savitskii, O. D. Christyakov, and T. M. Shkatova, Fiz. Tverd. Tela (Leningrad) **23**, 2827 (1981), [Sov. Phys.—Solid State **23**, 1652 (1981)].
- ²¹J. C. Fuggle, F. U. Hillebrecht, Z. Zolnierok, R. Lässer, Ch. Freiburg, O. Gunnarsson, and K. Schönhammer, Phys. Rev. B **27**, 7330 (1983).
- ²²E. Wuilloud, B. Delley, W. D. Schneider, and Y. Baer, J. Magn. Mater. **47-48**, 197 (1985).
- ²³O. Gunnarsson and K. Schönhammer, Phys. Rev. Lett. **50**, 604 (1983); Phys. Rev. B **28**, 4315 (1983).
- ²⁴D. Malterre, G. Krill, J. Durand, and G. Marchal, J. Phys. (Paris) Colloq. **46**, C8-199 (1985).
- ²⁵A. Guessous, K. Matho, J. Mazuer, and J. Palleau, J. Non-Cryst. Solids **65**, 429 (1984); K. Matho, J. Magn. Mater. **47-48**, 119 (1985).
- ²⁶J. M. Lawrence, J. W. Allen, S. J. Oh, and I. Lindau, Phys. Rev. B **26**, 2362 (1982).
- ²⁷Among the most recent theoretical approaches of the magnetic impurity problem for Ce, see N. E. Bickers, D. L. Cox, and J. W. Wilkins, Phys. Rev. Lett. **54**, 230 (1985).
- ²⁸P. A. Doriot, H. J. Güntherodt, and L. Schlapbach, Phys. Lett. **37A**, 213 (1971); **38A**, 458 (1972).
- ²⁹S. Raaen and R. D. Parks, Solid State Commun. **48**, 199 (1983).
- ³⁰G. van Kalker, H. van Nassou, and F. R. de Boer, J. Magn. Mater. **47-48**, 105 (1985).
- ³¹M. Croft, F. Lu, M. E. Melczer, A. Zolanz, G. Hall, and E. G. Spencer, J. Magn. Mater. **47-48**, 115 (1985).
- ³²J. Röhler, D. Wohlleben, J. P. Kappler, and G. Krill, Phys. Lett. **103A**, 220 (1984).
- ³³E. Beaurepaire, G. Krill, J. P. Kappler, and J. Röhler, Solid State Commun. **49**, 65 (1984).
- ³⁴R. D. Parks, S. Raaen, M. L. den Boer, V. Murgai and T. Mihalisin, Phys. Rev. B **28**, 3556 (1983); S. Raaen and R. D. Parks, *ibid.* **32**, 4241 (1985).
- ³⁵V. A. Shaburov, A. E. Sovestnov, I. A. Markova, E. M. Savitskii, O. D. Chistyakov, and T. M. Shkatova, Fiz. Tverd. Tela (Leningrad) **23**, 2455 (1981) [Sov. Phys.—Solid State **23**, 1437 (1981)].
- ³⁶B. Andraka, J. Timlin, and T. Mihalisin, J. Magn. Mater. **47-48**, 96 (1985).
- ³⁷Y. Onuki, Y. Shimizu, and T. Komatsubara, J. Phys. Soc. Jpn. **53**, 1210 (1984); G. R. Stewart, Z. Fisk and M. S. Wire, Phys. Rev. B **30**, 482 (1984).
- ³⁸E. Gratz, E. Bauer, B. Barbara, Z. Zemirli, F. Steglich, C. D. Bredl, and W. Lieke, J. Phys. F **15**, 1975 (1985).
- ³⁹O. L. T. de Menezes, A. Troper, P. Lederer, and A. A. Gomes, Phys. Rev. B **17**, 1997 (1978).
- ⁴⁰F. D. M. Haldane, Phys. Rev. B **15**, 2477 (1977).
- ⁴¹While this paper was prepared, we were made aware of L_{III} -absorption systematics performed independently by another group. See R. A. Neifeld, M. Croft, T. Mihalisin, C. U. Segre, M. Madigan, M. S. Torikachvili, M. B. Maple and L. E. Delong, Phys. Rev. B **32**, 6928 (1985). The d -band-filling effect is experimentally evidenced by these authors in different ternary and pseudobinary Ce-based crystalline compounds.