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X-ray-absorption spectroscopy investigation of the martensitic structural transformation in the *R*Cu (*R*=rare earth) series

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We present an x-ray-absorption spectroscopy (XAS) investigation performed at the $L_{1,3}$ edges of the rare earth Y K edge and K and $L_{2,3}$ edges of copper in several R-Cu intermetallic compounds: RCu (R=Y,Gd,Tb), $Y_{1-x}Tb_xCu$, and $Y_{1-x}Tb_xCu_yAg_{1-y}$. XAS spectra at the different absorption edges evidence the apparition of a strong electronic perturbation in the systems after the martensitic transformation. The dynamics of the structural transformation is discussed in terms of the interplay between the modification of both d-band widening and s-d transfer pressure.

I. INTRODUCTION

During the last two decades a large body of research has been devoted to the structural and magnetic characterization of the equiatomic binary compounds between rare earths (R) and nonmagnetic metals (M).[1,2] The main reason for such an interest was motivated by the simplicity of both the exchange interaction and the crystallographic structures, making it possible to study the effect of the conduction electron on the magnetic ordering. Indeed, most of the RM compounds form in the CsCl, CrB, or FeB crystal structure.[3] In particular, the RCu compounds attain the orthorhombic FeB and the cubic CsCl structures for the light and heavy rare earths, respectively.[4] Within this series, GdCu is the first compound to form the CsCl structure at room temperature. However, early works reported a tendency for GdCu to transform into FeB structure at liquid-nitrogen temperature, reappearing the CsCl structure after a suitable heat treatment.[4–6] The occurrence of such a large distortion of the cubic structure was confirmed by independent electrical resistivity, magnetic susceptibility, and thermal-expansion measurements that also report a similar behavior in TbCu and YCu compounds.[7–11] In all the cases, these anomalies have been identified as corresponding to the existence of a martensitic structural transformation that takes place at around 250, 140, and 117 K, for GdCu, YCu, and TbCu, respectively. Recently, the low-temperature structure of YCu has been identified as the FeB-type orthorombic structure.[12]

In the case of TbCu, the distortion of the cubic structure takes place at the Néel temperature 117 K, so that it was initially associated to the onset of a collinear to noncollinear magnetic structure.[7] However, it has been established from neutron-diffraction experiments that the para-antiferromagnetic transition is independent of the martensitic transformation.[13–15] Indeed, upon dilution of Tb by Y and due to the weakening of the exchange interaction, a lowering of the magnetic ordering temperature is observed, whereas the structural transition shifts to higher temperature. These experimental findings outlined the nonrelevance of the magnetoelastic energy in driving this transition and they have been recently confirmed by transport-properties measurements.[16]

Consequently, it is possible to address the existence of an unique mechanism as the origin of the martensitic transformation in both magnetic ordered GdCu, TbCu, and paramagnetic YCu compounds.

The mechanism that drives the martensitic transformations in the RCu systems is not completely understood. However, before that the crystallographic structure of the low-temperature phase of YCu was determined, several authors tentatively assigned it to the energy gain in the d-electron system due to the splitting of the d bands in the low-symmetry phase.[10,11] The same effect was previously proposed to account for the martensitic transformations taking place in RAg series.[8,17] All these interpretations have been developed on the grounds of the so-called band Jahn-Teller effect.[18–21] The essential idea is that a lattice deformation partially removes the degeneracy of d subbands in the $5d6s$ bands of the rare earth causing a repopulation of the various subbands, and resulting in a lowering of the crystal free energy. Partial support to this hypothesis has been achieved by the results of energy-band calculations performed on YCu and YZn compounds that report a strong $4d$ character for the conduction electrons near the Fermi surface.[22,23] However, although nowadays the origin of these structural martensitic transformations is commonly explained in terms of the structural instability of the CsCl crystallographic phase along the series, through the onset of the d-band Jahn-Teller effect, no experimental evidence of such electronic changes has been reported to date.

In this work, we present a systematic x-ray-absorption spectroscopy (XAS) investigation performed at the $L_{1,3}$ edges of the rare earth Y K edge, and K and $L_{2,3}$ edges of copper in several R-Cu intermetallic compounds: RCu (R=Y,Gd,Tb) and $Y_{0.1}Tb_{0.9}Cu$. The main objective of the present investigation is to establish the modification of the electronic structure of these systems under the martensitic transformation. Moreover, we have also stud-

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ied the $Y_{0.2}Tb_{0.8}Cu_{0.8}Ag_{0.2}$ system in which the Ag substitution suppresses the onset of the martensitic transformation. The XAS technique provides a very valuable tool to study changes in the local and partial density of states around the Fermi energy. In this way, a first evidence of the electronic changes occurred under the structural transformation is provided, leading to a deeper insight into the role of these electronic instabilities as the main mechanism driving such a class of transitions.

II. EXPERIMENTAL SETUP AND DATA ANALYSIS

The polycrystalline samples of the RCu alloys were prepared with rare earth 99.9% purity and copper of 99.999%. Samples were prepared by arc melting the starting elements under purified Ar atmosphere. Both phase and structural analysis were performed on a standard x-ray diffractometer. The preparation details and the characterization of samples have been previously reported.[11,13]

X-ray-absorption experiments at the Cu K edge and at the Tb and Gd $L_{1,3}$ edges were carried out at the beam line XASIV of the storage ring DCI of LURE at Orsay. A double-crystal Si(111) monochromator was used and the storage ring operated at 1.8 GeV with an average current of 150 mA. Yttrium K-edge spectra were recorded on Beamline 7C of the Photon Factory[24] at the National Laboratory for High Energy Physics (KEK). The storage ring was operated with a positron energy of 2.5 GeV and a stored current of about 300 mA. The beamline 7C was equipped with a Si(111) fixed-exit-beam double-crystal monochromator which provides also sagittal focusing of the synchrotron radiation. Rejection of higher harmonics was achieved by detuning of the two parallel and independent crystals of the monochromator between 40 and 60%.

For the absorption measurements samples were prepared in a single homogeneous plate of material. This guarantees that the martensitic transformation takes place upon cooling, because the structural transition is suppressed on powdered samples.[13–15] Thickness and homogeneity of the samples were optimized to obtain the best signal-to-noise ratio giving a total absorption jump, $\Delta\mu x$, ranging between 0.3 and 0.9 as a function of the selected absorption edge. All the measurements were carried out at room temperature in the transmission mode. Both x rays incident on the sample and transmitted through it were monitored by using two independent ionization chambers with a N_2-Ar flowing gas mixture optimized for each energy range.

The experiments at the Cu $L_{2,3}$ edges were carried out at the SA32 station of the SUPER-ACO storage ring at LURE synchrotron radiation facility in Orsay. A double-crystal Beryl 1010 monochromator was used. The x-ray absorption was measured by detecting the emitted electrons by a chaneltron in the total yield mode.

The absorption spectra were analyzed according to standard procedures.[25] The background contribution from lower energy absorption edges, $\mu_B(E)$, was approximated according to the Victoreen rule, $\mu_B(E) = A/E^3 + B/E^4$,[26] and subtracted from the experimental spectrum $\mu(E)$. Spectra were then normalized to the absorption coefficient at high energy, $\mu(E) = [\mu(E) - \mu_B(E)]/\mu(100\text{ eV})$, to eliminate thickness dependence.

III. RESULTS AND DISCUSSION

A. Cu K-edge and $L_{2,3}$-edge XANES spectra

The normalized x-ray absorption near-edge structure (XANES) spectra recorded at the Cu K edge in the case of GdCu and TbCu are shown in Figs. 1(a) and 1(b), respectively, and compared to those of the FeB-transformed phase. In all the cases, the XANES spectra present a

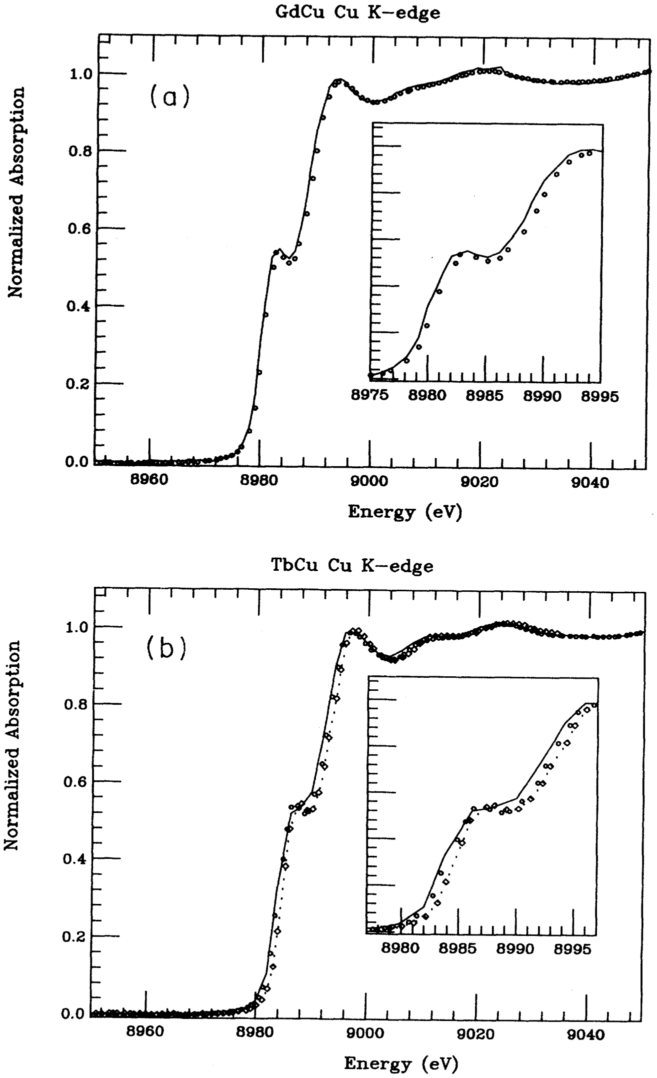

FIG. 1. Comparison between the experimental XANES spectra at the Cu K edge in the case of (a) GdCu (solid line) and its FeB-transformed phase (dots); (b) TbCu CsCl phase (solid line), FeB (dots) and DyCu (◇). In both panels, the insets report a more detailed comparison of the near-edge region.

steplike feature at the edge, that is similar to that of copper metal. This shape is characteristic of the existence of hybridization between the *p*-*d* conduction empty states at the Fermi level.[27] In both GdCu and TbCu, comparison of the absorption spectra before and after the martensitic transformation takes place exhibits marked differences just at the near-edge region. This region, extending over about 10 eV above the threshold, carries information about the unoccupied local and partial density of states of the system near the Fermi level.[27] The present XANES results reveal the existence of a large electronic perturbation of the system under the martensitic tranformation. Indeed, the Cu K-edge threshold is clearly shifted towards higher energy for the transformed phases, indicating that the Fermi level shifts toward higher energy. This result is an experimental confirmation of the electronic nature of this transformation which induces pronounced changes into the electronic structure of the system, thus supporting previous interpretations that addressed the important role of the character of the conduction electrons in driving this transformation.[8,10,11] In this sense, it is important to note the comparison of the Cu spectrum for DyCu and TbCu, shown in Fig. 1(b). Both DyCu and the FeB-transformed TbCu sample present a similar absorption profile that is shifted with respect to that of the TbCu in the cubic CsCl phase. Moreover, the Cu K-edge absorption threshold coincides in both DyCu and FeB-phase TbCu compounds. This steplike behavior can be related to the existence of two free-energy local minima in these systems, as proposed for Invar alloys,[28] corresponding to the CsCl and FeB phases, being the total energy of the system which determines the crystallographic phase. As the temperature decreases the FeB phase becomes energetically favored and the system evolves through a cubic-orthorhombic structural transformation.

Further verification of the existence of a shift of the Fermi level under martensitic transformation of the systems can be achieved by analyzing the copper $L_{2,3}$-edge absorption data. Figure 2 shows the absorption spectra at the Cu L_3 for a TbCu foil prior and after the martensitic transformation. In both cases, the absorption spectra show a step at the edge, contrary to all the other transition metals that display strong white lines corresponding to transitions to narrow 3*d* band.[29] This result is typical of metallic Cu, and corresponds to the presence of the atomic Cu $3d^{10}$ configuration.[29,30] Moreover, just below the absorption edge there is in both cases a small peak feature that corresponds to the presence of CuO on the sample surface. This peak provides the best reference to align the two spectra, which we have performed just at the maximum of this peak. After this procedure, it is made evident that the near edge is shifted towards higher energy in the case of the transformed, FeB-like, TbCu sample, and confirms the results obtained at the Cu K edge. At this point and in order to avoid any confusion, it should be noted that the increase of the CuO contribution to the absorption spectra in the transformed sample is merely an experimental artifact and it is not associated with the martensitic transformation. Indeed, although the experiment was performed on the same sample, the plate was removed from the experimental device and cooled down below the transition temperature. Thus, the observed increase of the CuO contribution can be attributed both to an additional oxidation on the sample surface and to the fact that the beam could hit a different region of the plate showing a higher oxidation.

Both Cu K- and $L_{2,3}$-edge XANES data address the presence of an electronic instability as the origin of such a structural transformation. In fact, although the number of conduction electrons in the system is keep constant, a net shift of the Fermi level is clearly detected. This result has been also verified in the case of YCu, Fig. 3 (a), as well as for the $Y_{0.1}Tb_{0.9}Cu$ and $Y_{0.2}Tb_{0.8}Cu_{0.8}Ag_{0.2}$ compounds. Figure 3(b) reports the comparison of the Cu K absorption edge in both systems, corresponding to the CsCl cubic phase. Upon substitution of Cu by Ag the transition has been observed to be suppressed.[10,13–15] As in the case of DyCu, which does not transform,

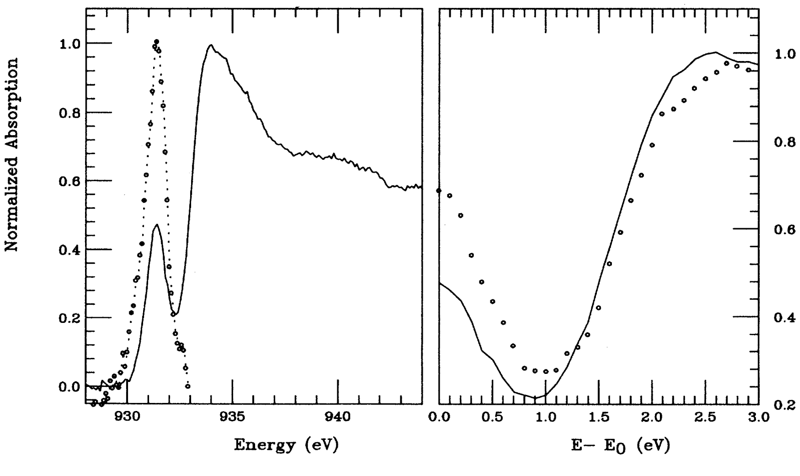

FIG. 2. Left panel reports the copper L_3-edge absorption in CuO (dots) and cubic TbCu (solid line). In the right panel the comparison of the L_3 XANES spectra for CsCl-(solid line) and FeB-TbCu samples (dots) is shown.

the $Y_{0.2}Tb_{0.8}Cu_{0.8}Ag_{0.2}$ threshold is also shifted towards higher energy, indicating that the new Fermi-level position overcomes the electronic instability that governs the volume change. This observation explains the stability of the CsCl structure for this compound in the entire range of temperature.

B. Y *K*-edge and rare earth $L_{1,3}$-edge XANES spectra

The precedent results can be verified by tuning the energy absorption at the rare earth or Y edges. Figure 4 reports the comparison of the absorption spectra at the Y *K* edge in the YCu system. Also at this edge it is found that the spectrum of the transformed sample is shifted towards higher energy as compared with that of the cubic CsCl phase. So far these results establish as an experimental fact the existence of Fermi levels with different energy for the two phases, a deeper insight on the dynamics of the process can be achieved from the study of the *L* edges of the rare earth. Indeed, in metals, the photoelectrons are scattered by the conduction electrons in the near-edge region (extending up to about 10 eV above the threshold, i.e., the photon energy of the core excitation to the Fermi level). Therefore, the final states of the photoelectron can be described as the unoccupied states close to the Fermi level so that the edge spectrum probes the unoccupied ground-state local and partial density of states of a given symmetry.[27]

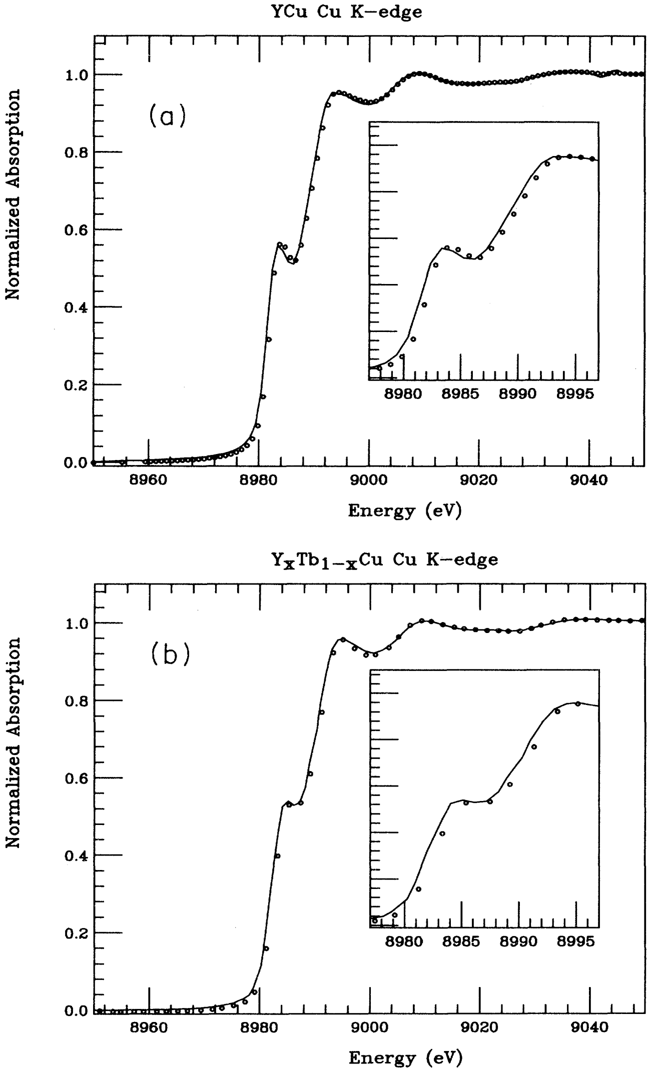

FIG. 3. Comparison between the experimental XANES spectra at the Cu *K* edge in the case of: (a) YCu (solid line) and FeB-transformed YCu (dots) compounds; (b) Cubic $Y_{0.1}Tb_{0.9}Cu$ (solid line) and $Y_{0.2}Tb_{0.8}Cu_{0.8}Ag_{0.2}$ (dots). In both cases a detailed comparison of the near-edge is reported in the inset.

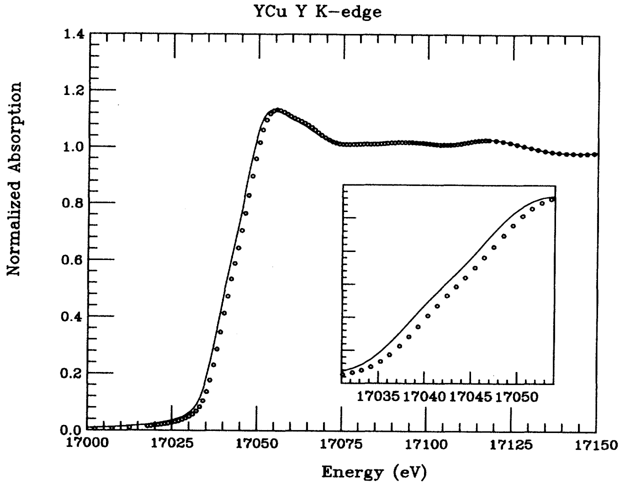

FIG. 4. Yttrium *K*-edge absorption spectra of YCu: cubic CsCl phase (solid line) and FeB-transformed (dots).

The proposed mechanism to explain the behavior of these alloys involves the energy modification in the system due to the splitting of the *d* bands in the low symmetry phase,[8,10,11] as it was earlier discussed to account for the martensitic transformations taking place in the *R*Ag series.[8,17] The underlying origin to this effect is that under a deformation of the crystal structure, the degeneracy of the 5*d* band of the rare earth in the cubic CsCl phase is removed. As a consequence, repopulation of the various subbands takes place and a decrease of the crystal free energy is achieved, so that the transformation to the new crystal structure is favored.[18–21] According to energy-band calculations performed on YCu and YZn, the Fermi level is supposed to be just below a sharp peak in the density of states (DOS) of mainly 4*d* character (the same is expected to hold with respect to 5*d* electrons in compounds of lanthanides),[22,23] so that under the occurrence of the so-called *d*-band Jahn-Teller effect noticeable modifications are expected to involve the *d* states in the vicinity of the Fermi level.

The absorption at the L_3 edge of the rare earth in these compounds is a very sound tool to study the behavior of the $5d$ band under the martensitic transformation and to verify the former hypothesis, by probing its impact upon the electronic structure of the systems. To this end, we have studied the absorption at the L_3 edge of the rare earth in both CsCl and FeB phases, as shown in Figs. 5(a) and 5(b) for GdCu and TbCu alloys, respectively. The spectra exhibit a pronounced peak at the absorption threshold, that corresponds to the atomic $2p \rightarrow 5d$ transition (white line). In the case of the FeB-transformed samples, the white line shows two variations with respect to that of the cubic, CsCl-like, TbCu, and GdCu compounds: the white line shifts toward higher energy and its intensity increases. The first effect confirms the shift of the Fermi level in the FeB orthorhombic phase. On the other hand, the increase of the white-line intensity indicates the existence of more d-symmetry empty states above the Fermi level at the R sites in the FeB crystal structure.

The fact that more accessible d states are detected in the FeB phase together with the shift of the Fermi level, without injection of additional electron to the system, supports, in a first approach, previous claims for the development of a d-band Jahn-Teller effect at the origin of the observed martensitic transformation. Within this framework, Ghatak, Ray, and Tannous have given an analytical expression for the onset of the martensitic transformation temperature T_M in a system with doubly degenerate electron bands.[21] The condition of appearance of T_M is given by $JN(E_F) > 1$, where J and $N(E_F)$ are the coupling constant between strain and energy bands, and the DOS at the Fermi energy, respectively. As a consequence, under the existence of a peculiar energy dependence of the DOS, an electronic instability is expected to occur in such a way that small modifications of external parameters, such as the chemical or hydrostatic pressure, can lead to the change of the Fermi-level position in the DOS and therefore, through the modification of $N(E_F)$, to the structural transformation of the system.

In this sense, the dependence of T_m in the RAg series upon chemical substitution has been qualitatively interpreted in terms of filling up the d band by assuming that E_F locates below the sharp peak of the DOS and that the substitution modifies both E_F and $N(E_F)$.[17,31] Moreover, when considering the pressure-induced modification of T_M, Kurisu and co-workers[31,32] have pointed out that there are two terms to be taken into account: the pressure-induced d-band widening that produces a decrease of $N(E_F)$, and the pressure-induced s-d transfer, that increases $N(E_F)$.[33] The different values of the critical pressure, p_c, in the RAg series have been accounted for by assuming that $N(E)$ or d-band occupancy increases with decreasing of the R atomic number.[31,34] Consequently, the condition for the appearance of the martensitic transformation can be satisfied only when the s-d transfer overcomes the d-band widening. Based on these experimental findings, Kadomatsu, Kurisu, and Fujiwara[32] formulated a hypothesis according to which the drastic structural transition is controlled by the character of the valence electrons of the rare earth, in such a way that whereas the s electrons favor cubic CsCl structure, the d electrons favor noncubic structures.

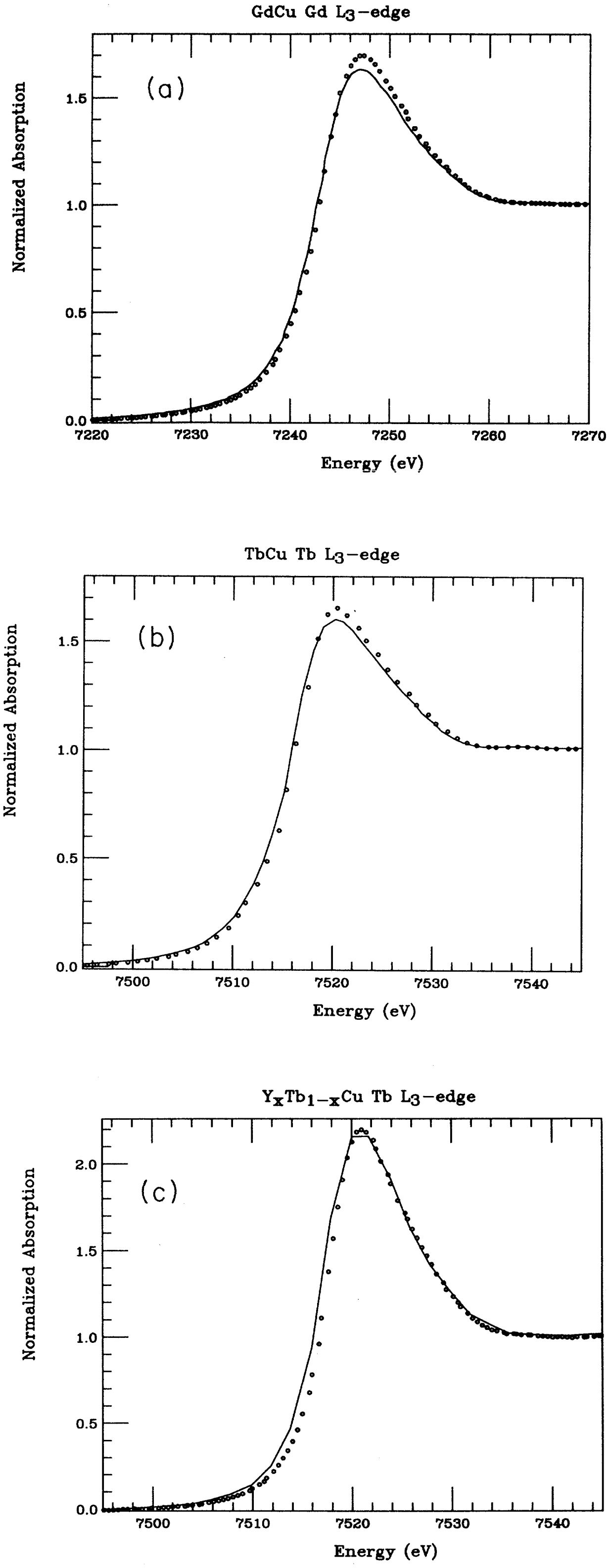

FIG. 5. Comparison between the experimental XANES spectra at the rare earth L_3 edge in (a) CsCl- (solid line) and FeB- (dots) GdCu compounds; (b) CsCl- (solid line) and FeB- (dots) TbCu; (c) cubic $Y_{0.1}Tb_{0.9}Cu$ (solid line) and $Y_{0.2}Tb_{0.8}Cu_{0.8}Ag_{0.2}$ (dots).

Identical considerations were applied to the YCu system to explain its behavior under pressure. So far hydrostatic pressure produces a reduction of the transition temperature, in contrast to the case of the *R*Ag series, this behavior has been ascribed to a dominant role of the *d*-band widening effect over the *s*-*d* transfer effect in the *R*Cu series.[10] However, this assumption is not without controversy. In fact, this conclusion is in contradiction with the experimental results of copper substitution by Ni, Ga, and Ag in $YCu_{1-x}M_x$ compounds. In these systems, with increasing x the lattice constant decreases for M=Ni and increases for Ag and Ga. Therefore, the associated *d* widening (narrowing) for Ni (Ga, Ag) should lead to a decrease (increase) of $N(E_F)$. Consequently, according the Ghatak's criterion,[21] a decrease of T_M should be expected for Ni-substituted compounds and the contrary would hold for Ga and Ag derivatives, which is in contradiction with the experimental observations. However, if we consider the effect of the *s*-*d* transfer, the substitution should increase *s*-*d* transfer in Ni derivatives, thus favoring the structural transition, whereas it should decrease in the Ga- and Ag-doped systems favoring the maintenance of the CsCl phase, as experimentally observed.[10] The important role of the *s*-electron character in the conduction bands was early pointed out by van Dongen *et al.*, who reported that increasing Ga substitution up to $x = 0.03$ in the $GdCu_{1-x}Ga_x$ compounds the structural transformation is suppressed.[6] Moreover, low-temperature Mössbauer measurements on $GdCu_{1-x}Ga_x$ and $GdAg_{1-x}In_x$ suggested a decreasing density of *s*-like electrons in the conduction band with increasing x in both systems, a result that can be related to the increase of the *s*-*d* transfer.[38]

In order to obtain a deeper insight into the modification of the *s*-*d* transfer at the onset of the martensitic transformation, we have recorded the absorption XANES spectra at the L_1 edge of the rare earth in these systems.

As shown in Fig. 6, the spectral shape of the L_1 spectra in GdCu and TbCu, in both cubic and orthorhombic phases, exhibits a staircaselike rise of the absorption at the threshold, as for lanthanide metals.[35] This feature reflects the *sp*-projected density of states in the band structure of the conduction electrons. Contrary to the $L_{2,3}$ case, the white line is very weak in the L_1 spectra because the atomic resonances corresponding to the one-electron transition *s*-*p* are very weak, due to the small oscillator strengths of the *s*-*p* transitions.[36,37] Because of the local site sensitivity of the XAS technique, the excitation from 2*s* core levels (L_1) probes only the local density of the empty *p* states. In the case of rare earths these *p* states are strongly hybridized with the outer *s* and continuum states, so that the analysis of the L_1 spectra can provide direct information of the changes in the *sp* conduction band occurring at the onset of the structural transformation.

Under martensitic transformation of both TbCu and GdCu samples, the intensity of such structure is depressed, and at the same time that the absorption edge shifts towards higher energy. This behavior of the L_1 spectra is just the opposite found at the L_3 edge. Whereas more accessible *d* states are available in the FeB phase, the contrary is found to hold for the *sp* final states. According to the previous discussion, both results can be correlated, supporting a reduction of the *s*-*d* charge transfer. Moreover, the same results have been found in the case of the Cu-Ag substituted compounds which do not exhibit the martensitic tranformation. Therefore, the present XANES results evidence the strong influence of the *s*-*d* transfer into driving the structural transformation in these systems.

IV. CONCLUSIONS

The interpretation of the x-ray absorption spectra recorded at the rare earth $L_{1,3}$ edges, Y *K* edge, and Cu *K* and $L_{2,3}$ edges clarifies the origin of the structural changes occurred in the *R*-Cu intermetallic compounds: *R*Cu (*R*=Y,Gd,Tb) and $Y_{1-x}Tb_xCu$.

Experimental evidence of the electronic origin of the

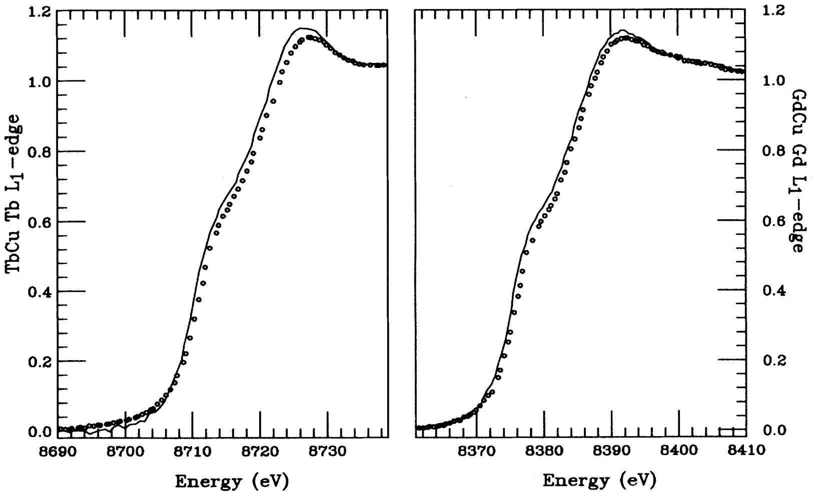

FIG. 6. Rare earth L_1-edge absorption in the cubic CsCl phase (solid line) and transformed FeB phase (dots) in TbCu (left panel) and GdCu (right panel).

martensitic transitions in these systems has been provided. XAS spectra at the different absorption edges evidence the shift of the Fermi level in the FeB-transformed samples. Our results are consistent with the onset of a d-band Jahn-Teller effect at the origin of these structural transitions.

The analysis of the XANES spectra at the $L_{1,3}$ edges of the rare earth, Y K edge, and K and $L_{2,3}$ edges of copper in the systems under investigation establish the modification of the electronic structure of these systems under the martensitic transformation. A net and steplike shift of the Fermi level has been observed in the case of the transformed samples. This behavior suggests the existence of two electronic states with different total energy in the system, as observed in Invar alloys, corresponding to the CsCl and FeB phases. The existence of two local minima close in energy and the location of the Fermi level near to a sharp peak in the DOS, results in a strong sensitivity of the Fermi-level position in these systems under small modifications of external parameters. As a consequence, a large effect of the hydrostatic pressure on the structural transformation is expected in all of these compounds.

From the analysis of the $L_{1,3}$ edges at the rare earth, an increase of the unoccupied d states and the decrease of the sp states above the Fermi level is found in both FeB-transformed samples and in the Ag-substituted samples that do not transform. These results indicate the relevance of the s-d hybridization into driving the cubic-orthorhombic transformation. The present XANES experiments strongly suggest that the modification of the electronic structure due to both d-band widening and s-d transfer is the key parameter governing the onset of the martensitic transformation of these systems.

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