Valence fluctuation in the dilute Eu systems Eu:RPd$_2$Si$_2$, Eu:RCu$_2$Si$_2$, and Eu:RNiSi$_2$ (R =La, Y, and Yb)

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^{151}Eu Mössbauer and L_3-edge measurements have been made on dilute europium alloys Eu$_{0.05}$Y$_{0.95}$Pd$_2$Si$_2$, Eu$_{0.05}$Yb$_{0.95}$Pd$_2$Si$_2$, Eu$_{0.05}$La$_{0.95}$Cu$_2$Si$_2$, Eu$_{0.05}$Yb$_{0.95}$Cu$_2$Si$_2$, Eu$_{0.05}$La$_{0.95}$NiSi$_2$, and Eu$_{0.05}$Y$_{0.95}$NiSi$_2$. We show that Eu ions exhibit valence-fluctuation phenomena in all these hosts. The valence of Eu ions in these hosts seems to be governed by their respective nearest-neighbor distance rather than unit-cell volume. Deviations from this behavior are pointed out and discussed.

I. INTRODUCTION

The phenomenon of valence fluctuations (VF) has been widely studied[1,2] in stoichiometric compounds where ambivalent rare-earth (R) atoms are one of their constituents and, therefore, have spatial periodicity.

Out of a few stoichiometric Eu-based VF systems that are known so far, EuPd$_2$Si$_2$ has been studied extensively. In this compound, average valence of Eu ions undergoes a large change ($\bar{v} = 2.2$ to 2.9) in a narrow range of temperature, around 150 K.[3] This rather sharp valence transition in this material has been taken as evidence of a cooperative valence transition driven by Eu-Eu interaction. Cooperative nature of the valence transition of EuPd$_2$Si$_2$ also follows, although indirectly, from the fact that Eu atoms, doped in an isostructural and analogous system LaPd$_2$Si$_2$ in dilute concentration, do exhibit valence fluctuation,[4] but the relatively sharp valence of EuPd$_2$Si$_2$ is absent. The variation of the average valence with temperature is rather gradual in Eu:LaPd$_2$Si$_2$.

Measurements of Bittins *et al.*[5] suggested that the VF behavior of Eu-ions introduced as impurity in YCu$_2$Si$_2$ is very similar to that in the stoichiometric compound EuCu$_2$Si$_2$. These authors pointed out that there are

quantitative but no qualitative differences in the valence change of Eu impurities in YCu$_2$Si$_2$ and that of Eu in EuCu$_2$Si$_2$ over the whole temperature range from 0 to 700 K. From their studies, they concluded that the valence fluctuation is a very local (atomic) phenomenon.

In view of this rather different behavior of valence fluctuation of Eu atoms in the two cases, we considered it essential to investigate the phenomenon of valence fluctuation of Eu ions introduced in dilute limit in several hosts. If a rare-earth atom, introduced as an impurity atom in a host lattice, exhibits valence fluctuation, it would imply that the host lattice itself has the essential ingredients that are conducive to the phenomenon of valence fluctuation and that spatial periodicity of Eu ions is not a necessity for sustaining valence fluctuation. This is significant as in stoichiometric systems, one is inclined to take the view that the constituent VF rare-earth atoms themselves collectively may be responsible for promoting the phenomenon of valence fluctuation.

We present here results of our ^{151}Eu Mössbauer and L_3 x-ray absorption edge measurements on a number of dilute Eu systems: Eu:YPd$_2$Si$_2$, Eu:YbPd$_2$Si$_2$, Eu:LaPd$_2$Si$_2$, Eu:LaCu$_2$Si$_2$ and Eu:YbCu$_2$Si$_2$, Eu:LaNiSi$_2$ and Eu:YNiSi$_2$.

II. SAMPLE PREPARATION

Master alloys of $R\text{Pd}_2\text{Si}_2$ (R = La, Eu, Yb), $R\text{Cu}_2\text{Si}_2$ (R = La, Eu, Yb), and $R\text{NiSi}_2$ (R = La, Eu, Y) were prepared by standard arc and/or induction melting technique. Loss of Eu was compensated by adding appropriate excess amount of europium while melting the alloys. Resulting ingots were sealed in evacuated quartz capsules and annealed at 900 K for about two weeks. After ensuring that master alloys were formed, the dilute Eu systems were then prepared by taking requisite amounts of the constituent master alloys and remelting them several times in induction furnace. Though, Eu loss was compensated while melting the alloys, compositions (with respect to Eu) reported here should be considered as nominal. Powder x-ray diffraction (XRD) measurements were carried out using a Siemens x-ray diffractometer.

III. EXPERIMENTAL TECHNIQUES

A. Mössbauer spectroscopy

Mössbauer spectroscopy is particularly important in studying valence state of Eu in Eu-based systems. Isomer shift (IS) of Eu nuclei in compounds containing stable divalent and trivalent Eu ions falls in two nonoverlapping ranges, viz., $S_2 \approx -8$ mm/sec to ≈ -12 mm/sec and $S_3 \approx 0$ mm/sec to $\approx +4.0$ mm/sec, respectively.[6] Usually, the fluctuation frequency of valency is of the order of 10^{-13} sec which is much smaller than the probing time of Eu Mössbauer resonance ($\approx 10^{-9}$ sec) which results in a dynamically averaged single Mössbauer line characterized by an IS intermediate between S_2 and S_3 (of suitably chosen reference compounds in which Eu ion is in stable divalent and trivalent state). Treating the system on the basis of the two-level phenomenological model[7] (with Eu^{3+} as the ground state and Eu^{2+} as the excited state separated by an energy, E_{ex}, and each level having a fluctuation broadening T_{sf}) the IS of the VF system, $S(T)$, at any temperature T can be expressed as,

$$S(T) = P_2(T)S_2 + P_3(T)S_3,$$

where S_2 and S_3 are the IS's of ^{151}Eu nucleus for stable Eu^{2+} and Eu^{3+} ions in suitably chosen compounds and $P_2(T)$ and $P_3(T)$ are the relative probabilities of occupation of the two valence states obtained by the usual Boltzmann statistics to the problem.[7] $P_2(T)$ and $P_3(T)$ contain explicitly the valence fluctuation parameter E_{ex} and T_{sf}. Temperature dependence of the average valence given by $\bar{v}(T) = 2P_2(T) + 3P_3(T)$ can be easily studied by measuring IS as a function of temperature, in a convenient and a straightforward manner. The reference IS values for S_2 and S_3 used in this work are $S_3 = 0.5$ mm/sec (IS of EuNi_2Si_2) for all the systems; $S_2 = -10.4$ mm/sec (IS of EuAg_2Si_2) for the EuPd_2Si_2 and EuCu_2Si_2 systems and $S_2 = -9.5$ mm/sec (IS of EuNiSi_3) for the EuNiSi_2 system as we do not have any other reference of isostructural Eu material.

B. L_3 x-ray absorption spectroscopy

Position of L_3 x-ray absorption edge of Eu is sensitive to the valency of Eu as the energy of the initial $p_{3/2}$ state depends upon the number of electrons in the $4f$ shell. The difference in the edge positions for divalent and trivalent Eu ions is about 6–8 eV (Ref. 8) and, therefore, the edges corresponding to the two valence states in a valence fluctuating compound are easily resolved. One observes two distinct and well resolved edges (not an averaged and collapsed single line as in the case of Mössbauer spectrum of VF compound) as the probe time of this technique is much smaller ($\approx 10^{-16}$ sec). Analysis of the observed edge profile[9] gives directly the populations of the two valence states. An interesting aspect is that even with rather low Eu concentration (and consequently an increase of the noise) the existence of the two structures is evidenced and can be reasonably fitted.

C. dc magnetic susceptibility

In principle, magnetic susceptibility of Eu-based materials should be very relevant in obtaining information with respect to the population of the two valence states. This is because magnetic susceptibility of the two ionic states of Eu, $4f^6$ and $4f^7$, are quite different. The ground state of the former configuration has $J = 0$ and, therefore, is nonmagnetic. The latter configuration has $J = \frac{7}{2}$ with an effective magnetic moment of $7.93\mu_B$. In the presence of VF one gets a population averaged magnetic moment corresponding to the average valence at any given one temperature.

Measurements of magnetic susceptibility, however, suffer from a number of shortcomings, in the context of systems containing VF ions in dilute limit. Traces of "stable" divalent Eu ions give rise to sizable contribution which is overwhelmingly large at low temperatures, and therefore, renders it difficult to estimate the contribution from the VF ions. Another source of uncertainty is that due to the relatively volatile nature of Eu, it is quite difficult to precisely control the concentration of the Eu ions in dilute alloys. Further, in those alloys such as $\text{Yb}_{1-x}\text{Eu}_x\text{Cu}_2\text{Si}_2$ and $\text{Yb}_{1-x}\text{Eu}_x\text{Pd}_2\text{Si}_2$, that contain two VF ions [Yb is in VF state in YbCu_2Si_2 (Ref. 7) and in YbPd_2Si_2], it is difficult to estimate the individual contributions arising from Yb and Eu ions. In view of such uncertainties, we believe that the magnetic susceptibility measurements would not obtain a definite information about valence state of the doped ion.

^{151}Eu Mössbauer measurements were made against a ^{151}Eu source in SmF_3 host matrix and using a home-built[10] constant acceleration spectrometer in conjunction with a microprocessor-based multichannel analyzer. All IS values reported here are with respect to EuF_3. L_3-edge studies of Eu were performed at the French Synchrotron Facility LURE, Orsay.

IV. RESULTS

X-ray diffraction patterns showed that all the materials investigated were single phase and had the ex-

TABLE I.   Unit-cell volume of Eu:RPd_2Si_2 (R =La,Eu,Y,Yb), Eu:RCu_2Si_2 (R=La,Eu,Y,Yb), and Eu:$RNiSi_2$ (R =La, Eu, Y) and the average valence (av. valency) of Eu at 300 K in these compounds [from Mössbauer isomer shift (IS) and from L_3 x-ray absorption edge (L_3) measurements].

Sample	Unit-cell volume (A^3)	Av. Valency (300 K)	
		IS	L_3
$Eu_{0.05}La_{0.95}Pd_2Si_2$	178.16	2.34	2.28
$EuPd_2Si_2$	175.21	2.26	2.25
$Eu_{0.05}Y_{0.95}Pd_2Si_2$	167.59	2.66	2.57
$Eu_{0.05}Yb_{0.95}Pd_2Si_2$	165.45	2.59	2.67
$Eu_{0.05}La_{0.95}Cu_2Si_2$	171.06	2.33	2.29
$EuCu_2Si_2$	165.12	2.60	2.6[a]
$Eu_{0.05}Y_{0.95}Cu_2Si_2$	156.73	2.54[b]	
$Eu_{0.05}Yb_{0.95}Cu_2Si_2$	153.93	2.59	2.64
$Eu_{0.05}La_{0.95}NiSi_2$	285.90	2.40	2.44
$EuNiSi_2$	275.73	2.71	2.62
$Eu_{0.05}Y_{0.95}NiSi_2$	261.80	2.7	

[a] Reference 23.
[b] Reference 5.

pected structure, viz., Eu:RPd_2Si_2 and Eu:RCu_2Si_2 crystallizing in the $ThCr_2Si_2$-type tetragonal ($I4/mmm$) structure[11] and Eu:$RNiSi_2$ in the $CeNiSi_2$ type orthorhombic ($Cmcm$) structure.[12] Lattice constants and unit cell volumes of the parent materials are given in Table I. It is clear from the table that the lattice volume follows the usually observed lanthanide contraction.

(i) $EuPd_2Si_2$, $Eu_{0.05}Y_{0.95}Pd_2Si_2$, $Eu_{0.05}Yb_{0.95}Pd_2Si_2$, and $Eu_{0.05}La_{0.95}Pd_2Si_2$.

$EuPd_2Si_2$ is perhaps the most extensively investigated Eu-based VF compound. Figure 1 shows the variation of IS of Eu, the variation with temperature being largest of
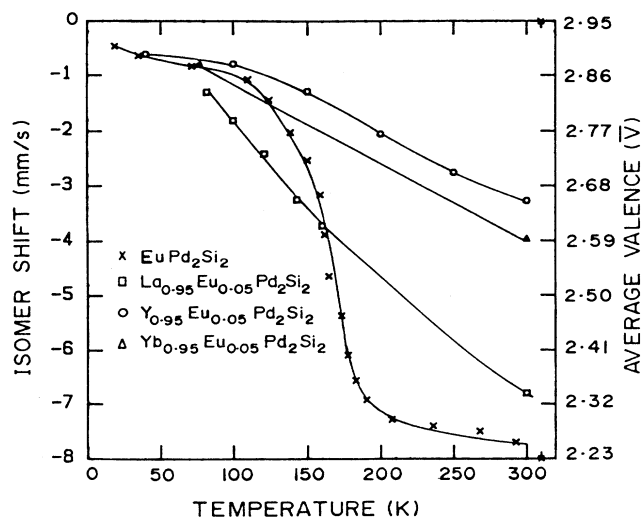
all the materials known so far. Also shown in this figure is the isomer shift in $Eu_{0.05}La_{0.95}Pd_2Si_2$.

Figure 2 shows the Mössbauer spectra of $Eu_{0.05}Y_{0.95}Pd_2Si_2$ at various temperatures. In both $Eu_{0.05}Y_{0.95}Pd_2Si_2$ and $Eu_{0.05}Yb_{0.95}Pd_2Si_2$ (not shown in the figure) samples only one absorption line is observed.

FIG. 1. ^{151}Eu Mössbauer isomer shift and average valence as a function of temperature of $EuPd_2Si_2$, $La_{0.95}Eu_{0.05}Pd_2Si_2$, $Y_{0.95}Eu_{0.05}Pd_2Si_2$, and $Yb_{0.95}Eu_{0.05}Pd_2Si_2$. Solid line through the data points is a guide to the eye. The data for $EuPd_2Si_2$ are taken from Ref. 24.
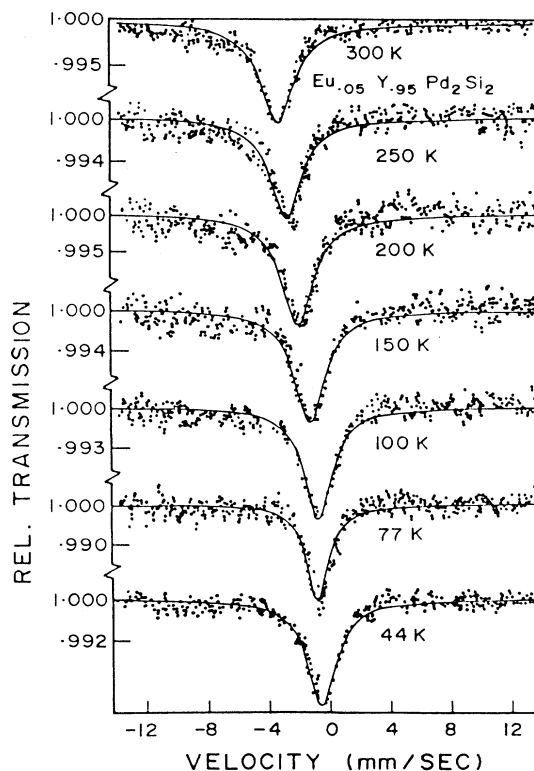

FIG. 2. ^{151}Eu Mössbauer spectra of $Eu_{0.05}Y_{0.95}Pd_2Si_2$ at various temperatures. Solid line is the Lorentzian fit.

A single Lorentzian line was fit to the spectra to extract the IS and the width of the line. As the width is found to be similar to what is usually observed which clearly suggests that the local environment of the doped Eu ions is quite alike. IS of the Eu ions observed in these cases does not fall in either of the two ranges belonging to the two stable ionic states mentioned earlier. Further, IS is temperature dependent. These observations show that Eu ions are in a VF state in these two dilute systems.

Average valence, $\bar{v}$, in the systems $Eu_{0.05}Y_{0.95}Pd_2Si_2$, $Eu_{0.05}Yb_{0.95}Pd_2Si_2$, and $Eu_{0.05}La_{0.95}Pd_2Si_2$ were calculated from the observed isomer shift data and using the relation given above. Values of $\bar{v}$, as a function of temperature, are shown in Fig. 1. Also are shown in the figure, IS and the $\bar{v}$ of Eu in the parent material $EuPd_2Si_2$ for the purpose of comparison. L_3 x-ray absorption edge spectra were measured in $Eu_{0.05}La_{0.95}Pd_2Si_2$, $Eu_{0.05}Y_{0.95}Pd_2Si_2$, and $Eu_{0.05}Yb_{0.95}Pd_2Si_2$ at 300 K and are shown in Fig. 3. These spectra exhibit a bimodal absorption, which is a characteristic feature of a VF system (provided there is only one crystallographic position of Eu atoms which, in fact, is true in the $ThCr_2Si_2$ structure). Statistical probabilities of the two valence states in the ground state of Eu ion were estimated following a deconvolution method.[9] Average valence calculated therefrom in these cases is given in Table I. We would like to point out that in the system $Eu_{0.05}Yb_{0.95}Pd_2Si_2$, Yb ion could be in a fluctuating state which in turn might affect to some extent the average valence of Eu.

L_3 x-ray absorption spectra were measured at 40 K also for the two materials $Eu_{0.05}Y_{0.95}Pd_2Si_2$ and $Eu_{0.05}La_{0.95}Pd_2Si_2$. In both the cases, intensity of the absorption edge corresponding to 3^+ increases at the cost of that corresponding to 2^+. This observation (temperature-dependent intensities of the 2^+ and 3^+ features in the absorption spectra) is consistent with the dynamic temporal valence fluctuations rather than the static spatial valence fluctuations such as arising from inequivalent crystallographic sites. In the latter situation, intensities of the two features would have been largely temperature independent. It must be emphasized here that L_3-edge measurements definitely indicate the VF state of this material at 300 K, though the valence is close to 2^+.

(ii) $EuCu_2Si_2$, $Eu_{0.05}La_{0.95}Cu_2Si_2$,   and $Eu_{0.05}Yb_{0.95}Cu_2Si_2$.

^{151}Eu isomer shift in the Eu-doped systems $Eu_{0.05}La_{0.95}Cu_2Si_2$ and $Eu_{0.05}Yb_{0.95}Cu_2Si_2$ along with that of $EuCu_2Si_2$ is shown in Fig. 4 as a function of temperature. Eu ions exhibit mixed valence behavior as is clear from the intermediate IS observed in these cases. $\bar{v}$ calculated from the isomer shift data, as a function of temperature, for these materials is shown in Fig. 4.

L_3-absorption edge spectra were measured in $Eu_{0.05}La_{0.95}Cu_2Si_2$ and $Eu_{0.05}Yb_{0.95}Cu_2Si_2$ at 300 K and 18 K. In both cases, there was bimodal absorption profile indicating the presence of mixed valence of Eu ions. Low-temperature spectra (see above our results of the L_3-absorption edge spectra of the dilute Pd-based compounds) suggested the shift of valence towards 3^+.

Analysis of the spectra led to the values of $\bar{v}$ which are given in Table I.

(iii) $EuNiSi_2$, $Eu_{0.05}La_{0.95}NiSi_2$, and $Eu_{0.05}Y_{0.95}NiSi_2$.

Mixed valence properties of $EuNiSi_2$ were first reported by Nagarajan et al.[13] using Mössbauer technique. Our L_3-edge absorption studies at various temperatures led to
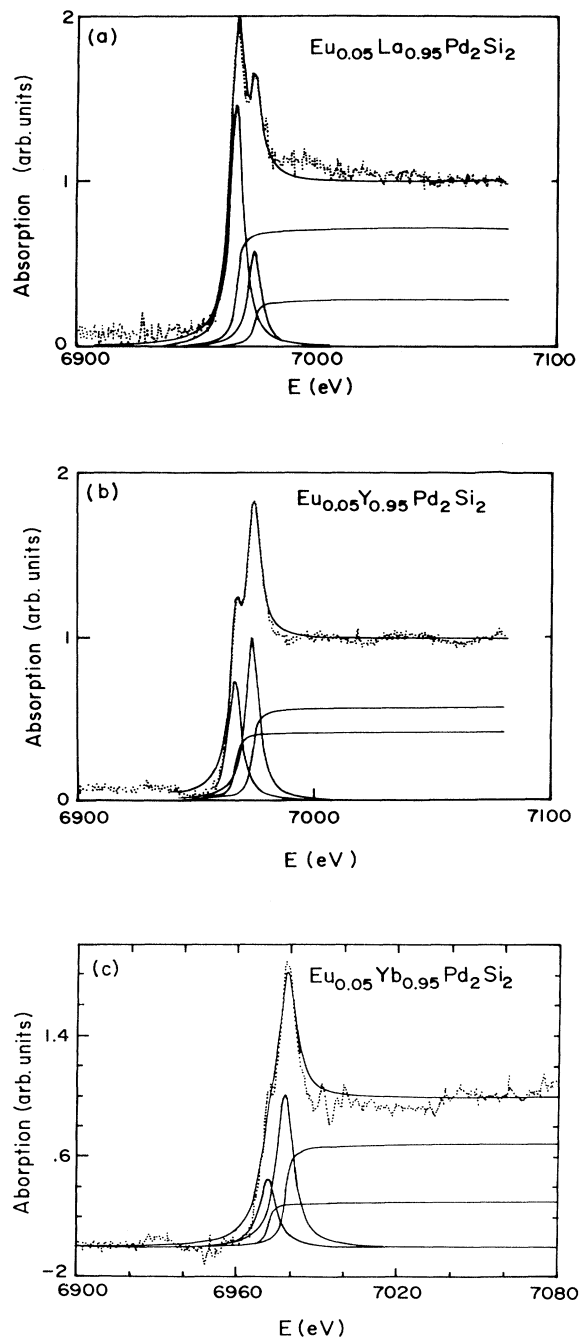

FIG. 3. L_3 x-ray absorption edge spectra of $Eu_{0.05}La_{0.95}Pd_2Si_2$, $Eu_{0.05}Y_{0.95}Pd_2Si_2$, and $Eu_{0.05}Yb_{0.95}Pd_2Si_2$ at 300 K. Solid line through data points is least-squares fit to the experimental data as described in the text.
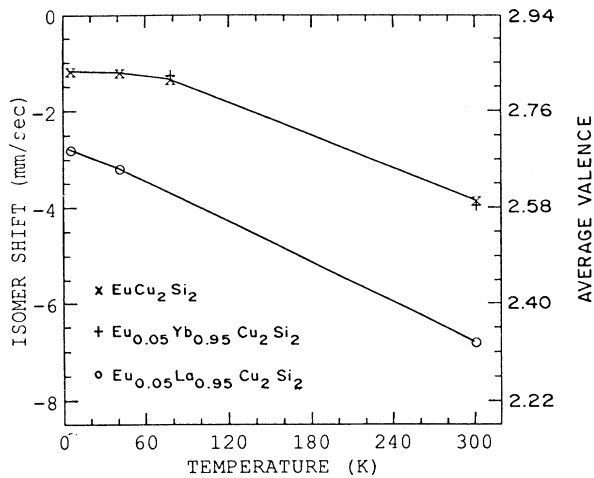
FIG. 4. ^{151}Eu Mössbauer isomer shift and average valence of EuCu$_2$Si$_2$, Eu$_{0.05}$Yb$_{0.95}$Cu$_2$Si$_2$, and Eu$_{0.05}$La$_{0.95}$Cu$_2$Si$_2$ as a function of temperature. Solid line through the data points is a guide to the eye.

further evidence to the existence of valence fluctuations in this material. $\bar{v}$ varies from 2.62 at 300 K to 2.75 at 6 K. It may be noted that in this case too there is only one type of Eu site.

Figure 5 shows Eu-Mössbauer spectra of EuNiSi$_2$, Eu$_{0.05}$La$_{0.95}$NiSi$_2$, and Eu$_{0.05}$Y$_{0.95}$NiSi$_2$ at 300 K. A very significant change of IS is clearly seen in Eu$_{0.05}$La$_{0.95}$NiSi$_2$ as compared to that in EuNiSi$_2$. Figure 6 shows the measured IS in the two dilute systems

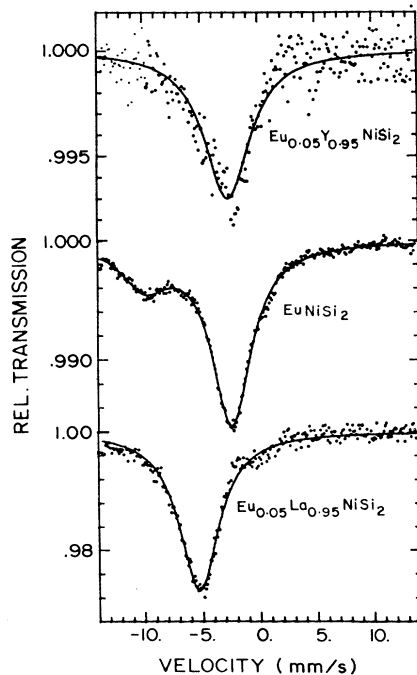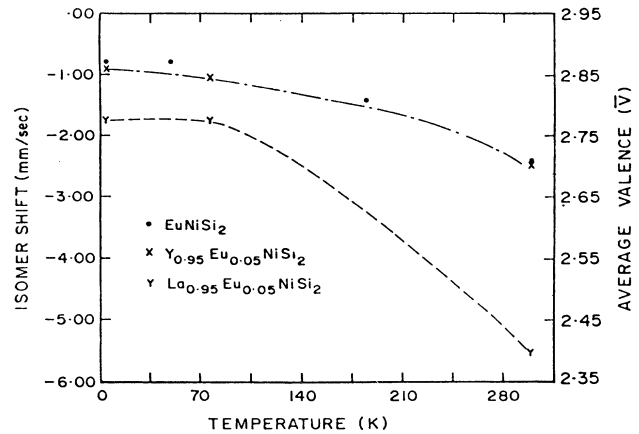FIG. 6. ^{151}Eu Mössbauer isomer shift and average valence as a function of temperature of EuNiSi$_2$, Y$_{0.95}$Eu$_{0.05}$NiSi$_2$, and La$_{0.95}$Eu$_{0.05}$NiSi$_2$. Dashed line and dot-dashed lines through the data points are guides to the eye.

as a function of temperature along with that of EuNiSi$_2$. $\bar{v}$ of Eu ions was deduced from the Mössbauer measurements in these two dilute materials Eu$_{0.05}$La$_{0.95}$NiSi$_2$ and Eu$_{0.05}$Y$_{0.95}$NiSi$_2$ and is plotted in Fig. 6.

L_3-absorption edge spectrum of europium was also measured in the dilute alloy Eu$_{0.05}$La$_{0.95}$NiSi$_2$ (Fig. 7). The L_3 is bimodal suggesting the presence of two ionic states of Eu. Analysis of the spectra was carried out as mentioned above and the information with respect to the valence state of Eu was extracted. These results are summarized in Table I.

V. DISCUSSION

From the measurements that we have been presented above, the following three features emerge.

(i) Eu ions *exhibit valence fluctuation* when introduced as impurity atoms in the host lattices RX_nY_m which

FIG. 5. ^{151}Eu Mössbauer spectra of Eu$_{0.05}$Y$_{0.95}$NiSi$_2$, EuNiSi$_2$, and Eu$_{0.05}$La$_{0.95}$NiSi$_2$ at 300 K. Solid line is the Lorentzian fit.
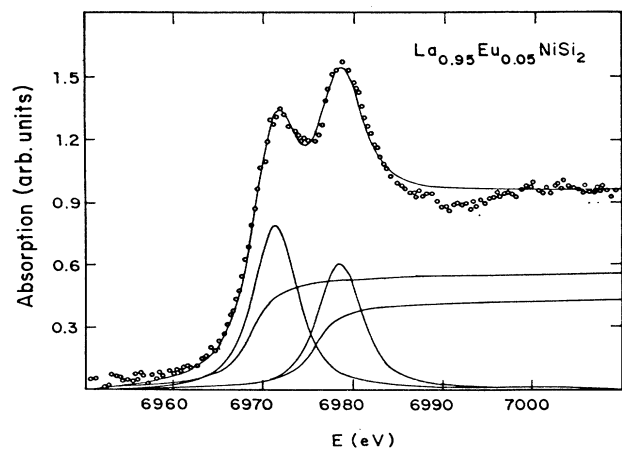

FIG. 7. L_3-absorption edge of La$_{0.95}$Eu$_{0.05}$NiSi$_2$ at 300 K. Solid line through data points is least-squares fit to the experimental data as described in the text.

are analogous and isostructural to an Eu-based VF compound EuX_nY_m. This implies that such host lattices have the essential ingredients to sustain valence fluctuations of the Eu atoms present in essentially single-atom limit and that concentration of Eu ions is not a necessity for sustaining VF. In this context, it is instructive to mention here the results of our L_3-edge measurements of Eu in $EuNi_2Si_2$. Eu is in stable 3^+ state in $EuNi_2Si_2$ as well as in $Eu:LaNi_2Si_2$. On the basis of cell volume alone, one would have expected Eu ions to be in VF state (or 2^+ state) in the latter material. One, therefore, infers that the lattice RNi_2Si_2 is not conducive for valence fluctuation. Continuing on the same line of argument, we point out that Eu is in VF state in $EuNi_2P_2$ (Ref. 14) and also in $Eu:YNi_2P_2$.[15]

(ii) The average valence of Eu atoms in La-based hosts shifts considerably towards 2^+ compared to that of Eu atoms in the parent Eu-based material. The case of $Eu:LaPd_2Si_2$ does not follow this trend and is discussed further below.

(iii) The average valence of Eu ions in Y-based hosts is very close to that of Eu in the parent compound. Here also, the case of $Eu:YPd_2Si_2$ does not follow this and is discussed further below.

It is known that the average valence of an ambivalent rare-earth ion in an intermediate valence compound can be changed either by chemical means, or by varying physical parameters such as the temperature and/or the pressure. For example, a small pressure (≈ 6.5 kbar) collapses SmS (Ref. 16) to a mixed valence state. SmS also undergoes a valence transition upon various chemical substitutions on Sm or S sites.[17] One usually understands variation of valence, in such cases, in terms of the unit-cell volume.

These considerations should also be applicable in the mixed valence behavior of the impurity Eu ions, introduced in various hosts that are isostructural to the parent Eu-based mixed valence compound. One would expect that expanded unit cell should sustain Eu ions closer to divalent state whereas the contracted unit cell should push the Eu atoms closer to being trivalent. As mentioned above (see Table I), this trend is observed in the cases of $Eu:LaCu_2Si_2$ and $Eu:LaNiSi_2$. The host lattices have larger unit cell than the respective parent lattice and the average valence v shifts towards 2^+. In the case of $Eu:LaPd_2Si_2$, however, even though the cell volume of the host is larger than that of the parent, the average valence of Eu is not shifted towards 2^+. It is important to point out, in this context, that these materials are highly anisotropic ($c/a \approx 3$) and the cell parameters may not vary in a similar manner (for instance, in $LaPd_2Si_2$ and $EuPd_2Si_2$, cell parameters a and c vary in opposite directions.[18] Additionally, in $EuPd_2Si_2$, a decreases and c increases with decrease in temperature[3]). *Unit-cell volume, therefore, is not always a useful parameter to predict the trend of variation of the valence. In such situations, one must also consider expansion or contraction of the immediate neighborhood of the atoms around the VF rare-earth ion.* In the two lattices, $LaPd_2Si_2$ and $EuPd_2Si_2$, Eu(La)-Si distances (Si atoms are the nearest neighbors of the rare-earth atoms) are essentially the same.[18] This, coupled with the fact that in the dilute alloy case also the $5d$, $6s$ electrons of Eu interact with $5d$, $6s$ electrons of La, it implies that the immediate neighborhood of the Eu ions is same in both the cases. Thus, it follows that valence state of Eu in $LaPd_2Si_2$ and in $EuPd_2Si_2$ should be similar which is consistent with what is observed.

In the contracted host lattices of $Eu:YbCu_2Si_2$ and $Eu:YNiSi_2$, average valence *of Eu ions does not move closer to 3^+*, it is nearly the same as that in the parent material (see Table I and Figs. 3 and 5). This is similar to the situation in $Eu:YCu_2Si_2$ wherein almost no change in average valence was seen by Bittins *et al.*[5]

It is important to recall, at this point, the fact that bulk modulus of the host lattices containing trivalent rare-earth ions is larger than that of the isostructural hosts containing divalent rare-earth ions.[19] In fact, it has been argued that the bulk modulus, for a series of isostructural materials, varies linearly as a function of $\bar{v}/V$ where V is the molar volume.[19] This forms the basis of the success of the Vegard's law. In mixed valence compounds, it is known that the Vegard's law breaks down and, if applied to VF compounds, overestimates the valence.[20] We believe that this may be the reason why in the contracted host lattices, valence of Eu is not larger than in the parent compound, for instance, compare the $\bar{v}$ of Eu in $EuNiSi_2$ and in $Y:EuNiSi_2$. This interpretation is further amply supported by the observed behavior of Eu ions introduced in YPd_2Si_2. At high temperatures, the average valence of Eu in $EuPd_2Si_2$ is ≈ 2.2 and, therefore, is quite susceptible to the lattice contraction which results in a higher valence in YPd_2Si_2. In the low-temperature end, however, there is no substantial difference in the average valence in these two cases for the same reasons mentioned just above.

VI. CONCLUSIONS

We have presented here results of our measurments of the average valence of Eu ions introduced in low concentration in many hosts, namely, $Eu:RPd_2Si_2$, $Eu:RCu_2Si_2$, and $Eu:RNiSi_2$ ($R = $ La, Y, and Yb). We have shown that Eu ions are in intermediate valence state in all of these systems. A common feature of these hosts is that they all are analogous and isostructural to a stoichiometric Eu-based mixed valent material. The fact that all of them support valence fluctuation implies that the structure of these hosts has the necessary ingredients to sustain mixed valence. The nearest-neighbor environment, *vis-a-vis* the unit cell volume, plays a key role in controlling the mixed valence of the Eu-impurity ions. In another situation, stable trivalent Eu in $EuPd_3$ could be transformed into the mixed valent state by introducing, in the matrix, "light" atoms such as Be, B, and Si. It has been inferred from EXAFS measurements,[21] in the case of $EuPd_3X_y$ ($X = $ Be, B, Si), that the regidity of the local environment is also affected on the introduction of the light atoms.

In many cases that we have studied here, volume con-

traction or expansion is effective in pushing the valence of Eu ions towards 3^+ or 2^+, respectively, upto a certain extent, beyond which the average valence becomes rather insensitive to the further variation of the lattice cell volume. This is a consequence of the failure of Vegard's law in mixed valence compounds. A similar effect has been noted in SmB_6 in which Sm valence smoothly increases from about 2.8 to 2.9 under external pressure but does not become fully trivalent as this process becomes harder as trivalent Sm is approached.[22]

ACKNOWLEDGMENT

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