# Charge Fluctuations and Local-Environment Dependence of the Energy of the 4f Virtual Localized Level of Eu in $Eu_x \, La_{1-x} \, Rh_2$†

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The recoilless-absorption spectra of the 21.6-keV $\gamma$ rays of $Eu^{151}$ in $Eu_x La_{1-x} Rh_2$ are composed of a few lines which exhibit strongly temperature-dependent isomer shifts. The results are interpreted in terms of fast fluctuations of electrons between a localized 4f level and the conduction band. The energy released by removing an electron from the 4f level to the conduction band (0.01–0.1 eV) depends significantly on the number of La nearest neighbors. The levels have a width of $\sim 0.01$ eV.

We report here recoilless-absorption studies of the 21.6-keV $\gamma$ ray of $Eu^{151}$ in $Eu_x La_{1-x} Rh_2$ and in $Eu_{0.125} Pr_{0.875} Rh_2$. The absorbtion spectra are composed of a few lines which exhibit strongly temperature-dependent isomer shifts. Each line of a spectrum is attributed to a different Eu site characterized by the number of La nearest neighbors (0, 1, 2, 3, or 4). The results are interpreted in terms of fast fluctuations of electrons between a localized 4f level and the conduction band, leading to a fluctuating charge density at the Eu nuclei.[1-3] Our present results show that $E_{exc}$, the energy necessary to make an interconfiguration excitation from $4f^6$ to $4f^7$ by removing an electron from the conduction band at the Fermi energy $E_F$ and placing it in the localized 4f level, is very small (0.01–0.1 eV) and depends very significantly on the number of La (or Pr) nearest neighbors. Thus, for example, the values of $E_{exc}$ in $Eu_{0.125} La_{0.875} Rh_2$ at temperatures above 80 K were found to be 0.0065, 0.32, and $\sim 0.1$ eV for Eu ions with 4, 3, and 2 La first-nearest neighbors, respectively. The present results also show that the localized 4f levels in the compounds investigated have energy widths of about 0.01 eV.

Charge-fluctuation effects have recently been observed in the Mössbauer spectra of $EuCu_2Si_2$.[3] It was pointed out in Ref. 3 that nonunique charge states of Eu ions may be expected in other systems whenever the unit cells have intermediate values between those for which the Eu ions are trivalent and those for which the Eu ions are divalent. In the europium Laves-phase compounds ($EuM_2$ compounds with the $MgCu_2$ structure) with large unit cells (e.g., in $EuAl_2$ with $a = 8.11$ Å or in $EuPt_2$ with $a = 7.73$ Å) the Eu ions are divalent. In $EuM_2$ compounds with relatively small unit cells (e.g., in Eu in $SmFe_2$ with $a = 7.40$ Å) the Eu ion is trivalent. It was therefore expected that in $EuM_2$ compounds with intermediate unit cells ($7.4 < a < 7.7$ Å) phenomena associated with non-unique charge states would be observed. The $Eu_x La_{1-x} Rh_2$ and the $Eu_x Pr_{1-x} Rh_2$ compounds have such intermediate unit cells and were therefore chosen as absorbers. Phenomena associated with nonunique charge states of Eu ions were indeed found in these systems.
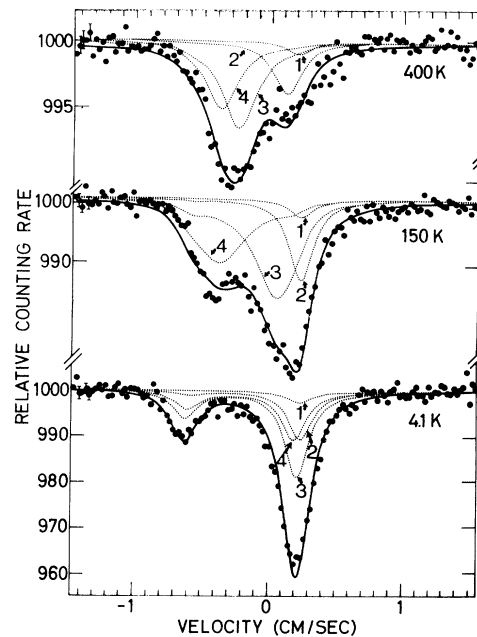
Recoilless-absorption measurements of the



FIG. 1. Recoilless-absorption spectra of the 21.6-keV $\gamma$ ray of $Eu^{151}$ in $Eu_{0.25} La_{0.75} Rh_2$. The solid lines are the theoretical best fits to the experimental spectra. The dotted lines are the theoretical subspectra, each of which corresponds to a different Eu site, characterized by $M$, the number of La nearest neighbors. The value of $M$ is marked near each dotted line. The subspectra corresponding to $M = 0$ are not shown in the figure as their relative intensity is very small. Each solid line is the sum of the dotted lines.

21.6-keV $\gamma$ ray of $Eu^{151}$ in $EuRh_2$, $Eu_{0.075}La_{0.925}Rh_2$, $Eu_{0.125}La_{0.875}Rh_2$, $Eu_{0.25}La_{0.75}Rh_2$, $Eu_{0.5}La_{0.5}Rh_2$, and $Eu_{0.125}Pr_{0.875}Rh_2$ were carried out at various temperatures between 4.1 and 500 K (for most of the compounds, the measurements were carried out at 4.1, 25, 70, 90, 150, 190, 240, and 400 K). The source used was $Sm^{151}F_3$ at room temperature. The compounds were prepared by melting stoichiometric amounts of the elements in an argon atmosphere with an induction furnace and annealling them for 24 h at 600°C.· The compounds crystallize in the cubic Laves-phase $MgCu_2$ structure. Crystallographically, all the rare-earth sites are equivalent. Some of the spectra obtained are shown in Fig. 1. The following features characterize the experimental spectra:

(a) In each of the $EuRh_2$ measurements a single absorption line was obtained. Its position changed continuously as a function of temperature from 2.4 mm/sec at 4.1 K to 0.4 mm/sec at 500 K. The changes in the isomer shifts are about 10 times larger than those produced by the temperature-dependent second-order Doppler effect.

(b) The spectra of the ternary compounds are composed of a few lines which correspond to inequivalent Eu sites. (c) At very low temperatures (4.1 K) the spectra of the ternary compounds are composed of two lines. One of the lines is at a velocity of $+2$ mm/sec, which is characteristic of $Eu^{3+}$ ions in metallic systems, and the second line is at a velocity of $\sim -6.5$ mm/sec, close to the velocities corresponding to $Eu^{2+}$ ions. At higher temperatures additional lines at velocities corresponding neither to divalent nor to trivalent Eu ions are observed.

(d) The isomer shifts of the various absorption lines vary continuously very significantly as a function of temperature.

All the present experimental results can be explained by the assumption of fast fluctuations of electrons between a localized $4f$ level of finite width $\Delta$, located at $E_{exc} = E_{4f}^{eff} - E_F$ above the Fermi level, and the conduction band. $E_{exc}$ and $\Delta$ are, at each temperature, functions of $M$, the number of La (or Pr) nearest neighbors ($M = 0$, 1, 2, 3, or 4).

The probability of an Eu ion to have $M$ La first-nearest neighbors in an $Eu_xLa_{1-x}Rh_2$ compound is given by

$$Q_M(x) = \binom{4}{M}x^{4-M}(1-x)^M. \tag{1}$$

The probability of the fluctuating electron to be in the conduction band (and thus produce a $4f^6$ configuration) is given by[4]

$$p(T, E_{exc}{}^M) = \{1 + 8[1 + 3\exp(-480/T) + 5\exp(-1330/T)]^{-1}\exp(-E_{exc}{}^M/kT)\}^{-1}. \tag{2}$$

This formula is equivalent to the formula given in Ref. 3 for $P_3$ (population of the $Eu^{3+}$ state) if $\Delta$ of Ref. 3 is identified with $E_{exc}$, defined in the present paper.

The isomer shift corresponding to the Eu ions which have $M$ La (or Pr) nearest neighbors will be given, in the fast-fluctuation limit, by

$$S(T, E_{exc}{}^M) = (S_3 - S_2)p(T, E_{exc}{}^M) + S_2, \tag{3}$$

where $S_2$ and $S_3$ are the isomer shifts corresponding to pure $Eu^{2+}$ and $Eu^{3+}$ states, respectively.

In order to get good fits to the experimental spectra, especially to those measured at very low temperatures, we had to assume that the $4f$ level has a finite energy width $\Delta_M$, which is a function of $M$, the number of La nearest neighbors. This width may represent the natural width of the $4f$ level or it may be produced by broadening due to inhomogeneity caused, for example, by the dependence of $E_{4f}$ on the number of La second-nearest neighbors.

If it is assumed that the energy of the $4f$ level has a Lorentzian distribution then the distribution in the value of $E_{exc}{}^M$ will be given by

$$D_M(E) = \frac{\Delta_M/\pi}{\Delta_M{}^2 + (E - E_{exc}{}^M)^2}; \tag{4}$$

then the expected Mössbauer spectrum will be given by

$$I(\omega) = \sum_{M=0}^{M=4} Q_M(x)\int_{-\infty}^{\infty} D_M(E)\frac{\Gamma/\pi}{\Gamma^2 + [\omega - S(T, E)]^2}dE, \tag{5}$$

where $\Gamma$ is the full width at half-maximum of the Mössbauer absorption line. $I(\omega)$ depends on ten free parameters: the excitation energies $E_{exc}{}^M$ and their widths $\Delta_M$ for $M = 0$, 1, 2, 3, and 4. For $x = 0.075$

TABLE I. Values of $E_{exc}$ derived from the analysis of the experimental spectra of $Eu_x La_{1-x} Rh_2$ compounds and $Eu_{0.125} Pr_{0.875} Rh_2$ (the energies are given in units of K).

| x | T (K) | $E_{exc}^4$ | $E_{exc}^3$ | $E_{exc}^2$ | $E_{exc}^1$ | $E_{exc}^0$ |
|---|---|---|---|---|---|---|
| 0.085 | 4.1-400 | $-100^{+}_{-}40$ | $150^{+}_{-}50$ | - | - | - |
| 0.125 | 4.1 | $20^{+}_{-}10$ | $100^{+}_{-}50$ | - | - | - |
| 0.125 | 15 | $30^{+}_{-}15$ | $140^{+}_{-}50$ | - | - | - |
| 0.125 | 25 | $35^{+}_{-}15$ | $150^{+}_{-}50$ | - | - | - |
| 0.125 | 45 | $45^{+}_{-}15$ | $270^{+}_{-}100$ | - | - | - |
| 0.125 | 90-400 | $75^{+}_{-}25$ | $370^{+}_{-}80$ | >1000 | - | - |
| 0.25 | 4.1 | $35^{+}_{-}20$ | $250^{+}_{-}50$ | - | - | - |
| 0.25 | 25 | $50^{+}_{-}20$ | $250^{+}_{-}50$ | - | - | - |
| 0.25 | 70 | $100^{+}_{-}30$ | $350^{+}_{-}50$ | - | - | - |
| 0.25 | 80-400 | $200^{+}_{-}30$ | $550^{+}_{-}50$ | >1100 | >1100 | - |
| 0.5 | 4.1 | $25^{+}_{-}10$ | $130^{+}_{-}50$ | - | - | - |
| 0.5 | 89 | $75^{+}_{-}30$ | $300^{+}_{-}50$ | - | - | - |
| 0.5 | 100-400 | $180^{+}_{-}40$ | $450^{+}_{-}100$ | $850^{+}_{-}200$ | >1100 | >1100 |
| 1.0 | 4.1-500 | - | - | - | - | $1100^{+}_{-}200$ |
| $Eu_{1/8} Pr_{7/8} Rh_2$ | 80-400 | $550^{+}_{-}40$ | $1300^{+}_{-}200$ | >1300 | - | - |

and 0.125, practically only the six parameters corresponding to $M=2$, 3, and 4 have to be taken into account.

For $T=0$, $S(0,E)$ equals $S_3$ for $E>0$ and $S_2$ for $E<0$. For such a case, $I_0(\omega)$ has the form

$$I_0(\omega) = \sum_{M=0}^{M=4} Q_M(x) \left( \frac{\Gamma}{\pi} \frac{\frac{1}{2} - \pi^{-1} \arctan(E_{exc}^M/\Delta_M)}{\Gamma^2 + (\omega - S_2)^2} + \frac{\Gamma}{\pi} \frac{\frac{1}{2} + \pi^{-1} \arctan(E_{exc}^M/\Delta_M)}{\Gamma^2 + (\omega - S_3)^2} \right). \tag{6}$$

From formula (6), it is clear that at $T=0$ only two absorption lines, one corresponding to the pure $Eu^{2+}$ configuration and the other corresponding to the pure $Eu^{3+}$ configuration, should be observed. This is essentially what is observed in all the 4.1-K spectra (Fig. 1).

Least-squares computer fits to all the experimental spectra were made by using Eq. (5). The values of the parameters $E_{exc}^M$ derived from these fits are summarized in Table I. The values derived for $\Delta_4$ varied between 40 and 80 K and the values for $\Delta_3$ varied between 60 and 150 K. The values of $\Delta_2$ and $\Delta_1$ were larger than 200 K. The solid lines in Fig. 1 are the theoretical fits to the experimental spectra. The dotted lines correspond to different Eu sites characterized by $M$, the number of La nearest neighbors ($M=0$, 1, 2, 3, or 4). The values derived from

the analysis of the spectra for $S_2$ (isomer shift corresponding to the $Eu^{2+}$ configuration, relative to the $SmF_3$ source) varied between $-5.8$ and $-6.5$ mm/sec. The values derived for $S_3$ (isomer shift corresponding to the $Eu^{3+}$ configuration) varied between $+1.6$ and $2.4$ mm/sec. The value found for $S_2$ is somewhat different from the values found generally for divalent intermetallic compounds of Eu ($\sim -8$ mm/sec). This may indicate that, as a result of the small separation between the $4f$ localized level and the Fermi level, the configuration of the $Eu^{2+}$ state in $Eu_x La_{1-x} Rh_2$ is not a pure $4f^7$ configuration.

It follows from Table I that the values of $E_{exc}^M$ above 80 K are almost temperature independent. At temperatures below 80 K, the values of $E_{exc}^M$ change significantly with temperature. The val-

ues of $E_{exc}^4$ and $E_{exc}^3$ at 4.1 K are about $\frac{1}{3}$ of their
values at 80 K. The dependence of $E_{exc}$ on tem-
perature is consistent with theoretical predic-
tions. $E_{exc}$ at low temperatures can be expressed
in the form[4]

$$E_{exc}(T) = E_{4f}^{eff} - E_F(T) = E_{4f}^{eff} - c(z + p)^{2/3}, \quad (7)$$

where $E_{4f}^{eff}$ is independent of $p$ or temperature,
$c$ is a positive constant, and $z$ is the number of
conduction electrons per ion for $p = 0$. The val-
ues of $E_{exc}^M$ for the $Eu_xLa_{1-x}Rh_2$ compounds were
found to be positive (except for $E_{exc}^4$ of $x = 0.075$)
and $p$ therefore decreases with temperature. Ac-
cording to Eq. (7) such a decrease will cause
$E_{exc}^M$ to be an increasing function of temperature,
as found from our analysis of the experimental
results.

In the analysis of the experimental results, it
was assumed that the widths of all the moving
lines do not change as a function of temperature,
and that they are equal to the linewidth in the ab-
sence of fluctuation phenomena. This assump-
tion implies that the characteristic fluctuation

time between the $4f$ localized level and the con-
duction band is shorter than $4 \times 10^{-11}$ sec. Such
short fluctuation times are consistent with the
values of 100 K found for the widths of the local-
ized $4f$ level. Such a width corresponds to a life-
time of $10^{-13}$ sec.

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# New Type of Phase Transition

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It is shown that the ferromagnetic Ising model on a Cayley tree lattice exhibits a new
type of phase transition at the field $B = 0$ below the Bethe–Peierls transition tempera-
ture $T_{BP}$. The leading nonanalytic part of the free energy is of the form $B^\kappa$, where the
"critical" exponent $\kappa(T)$ increases smoothly from one to infinity as the temperature
goes from 0 to $T_{BP}$. This implies a transition of "continuous" order $\kappa$.

The self-consistent Bethe–Peierls (BP) treat-
ment[1] has been believed to be exact for the ferro-
magnetic Ising problem on a Cayley tree (also
called Bethe lattice).[2] Only recently Eggarter[3]
found that the corresponding free energy at zero
magnetic field is an analytic function of the tem-
perature, thus implying no phase transition in
contrast to the BP treatment. As pointed out in
Ref. 3, the explanation of the apparent paradox
is the unusual topological structure of a large
Cayley tree: Not only is a finite portion of its
sites on the surface, but the "interior" of a Cay-
ley tree, i.e., all sites a sufficient distance
away from the surface, actually contains an ar-
bitrarily small portion of all the sites. The BP
transition, in fact, takes place only in the "in-

terior" and disappears if the bulk properties are
calculated in the proper thermodynamic limit.

In this paper we shall prove that the bulk be-
havior of the Ising model on a Cayley tree never-
theless displays a phase transition, but an un-
usual one. The transition is seen only in the field
dependence of the free energy and becomes arbi-
trarily weak, if the Bethe–Peierls transition tem-
perature $T_{BP}$ is approached from below. Since
this transition smoothly interpolates between a
first-order transition at $T = 0$ and an infinite-or-
der transition at $T_{BP}$, it might be called a con-
tinuous transition.

First we derive a closed expression for the
free energy per site in the thermodynamic limit.
For simple notation we use a reduced tempera-