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**MÖSSBAUER EFFECT STUDIES OF INTERCONFIGURATION FLUCTUATIONS IN METALLIC RARE EARTH COMPOUNDS (**)**

E. R. BAUMINGER, I. FELNER, D. FROINDLICH
D. LEVRON, I. NOWIK, S. OFER and R. YANOVSKY

The Racah Institute of Physics, The Hebrew University, Jerusalem, Israel

**Resumen.** — Los espectros de absorción sin recelo del rayo gamma de 21,6 keV de $^{151}$Eu en EuCu$_2$Si$_2$ y en EuRh$_2$ revelan un pic único donde el derrumbe isométrico depende fuertemente de la temperatura. Los espectros de Eu$_{1-x}$La$_x$Rh$_2$ (0,075 $\leq x \leq 0,5$), Eu$_{1,25}$Pr$_{0,75}$Rh$_2$ y Eu$_{1,25}$Pt$_{0,75}$Rh$_2$ (0,125 $\leq x \leq 1$) contienen varios picos, donde los derrumbes isométricos varían abruptamente con la temperatura. Cada raíz de estos espectros se atribuye a un sitio diferente de Eu, caracterizado por el número de proches voisins La, Pr o Pt. Los derrumbes isométricos de muchos de estos picos no se corresponden ni a Eu$^{2+}$ ni a Eu$^{3+}$, pero presentan valores intermedios. Todos los resultados son interpretados en términos de fluctuaciones rápidas ($r < 4 \times 10^{-11}$ s) entre las configuraciones 4f$^6$ y 4f$^7$. La energía necesaria a una excitación interconformational de un electrón de 4f$^6$ a 4f$^7$, en enlazando un electrón a la banda de conducción hasta el nivel de Fermi y el plaçant ensuite en el nivel 4f localizado, es de ~ 800 K en EuCu$_2$Si$_2$ y de ~ 1 200 K en EuRh$_2$. En los compuestos ternarios, esta energía depende notablemente del número de proches voisins La, Pr o Pt de Eu, y así ligeramente de la temperatura. Los niveles 4f localizados tienen una gran energía enmedio de 100 K. Los espectros de absorción sin recelo Yb metal del rayo gamma de 84 keV de $^{170}$Yb emitido por una de $^{170}$Tm$_2$Ho$_{1-x}$Fe$_2$ componen dos subspectros que tienen el presente 5 raíces y el otro es un pic claramente centrado alrededor de la vitesse zero. Estos espectros también se interpretan en términos de fluctuación interconformational (4f$^{14} \leftrightarrow 4f^{15}$).

**Abstract.** — Recoilless absorption spectra of the 21.6 keV gamma ray of $^{151}$Eu in EuCu$_2$Si$_2$ and in EuRh$_2$ reveal a single absorption line which has a strongly temperature dependent isomer shift. The recoilless absorption spectra in Eu$_{1-x}$La$_x$Rh$_2$ (0.075 $\leq x \leq 0.5$), Eu$_{1,25}$Pr$_{0,75}$Rh$_2$ and Eu$_{1,25}$Pt$_{0,75}$Rh$_2$ (0.125 $\leq x \leq 1$) are composed of a few lines, many of which also exhibit strongly temperature dependent isomer shifts. Each line in these spectra is attributed to a different Eu site characterized by the number of La, Pr or Pt nearest neighbors. The isomer shifts of many of the lines correspond to neither Eu$^{2+}$ nor Eu$^{3+}$ valencies, but fall in between. All the results are interpreted in terms of fast fluctuations ($r < 4 \times 10^{-11}$ s) between the 4f$^6$ and 4f$^7$ configurations. 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 level and placing it in the localized 4f level, is ~ 800 K in EuCu$_2$Si$_2$ and ~ 1 200 K in EuRh$_2$. In the ternary compounds, this energy depends significantly on the number of La, Pr or Pt nearest neighbors of the Eu ions, and is somewhat temperature dependent. The localized 4f levels have an energy width of about 100 K. The recoilless absorption spectra in Yb metal of the 84 keV gamma ray of $^{170}$Yb emitted by a $^{170}$Tm$_2$Ho$_{1-x}$Fe$_2$ source are composed of two subspectra, one of which is a 5 line split spectrum and the other is a broadened line at zero velocity. These spectra are also interpreted in terms of interconfiguration fluctuations (4f$^{14} \leftrightarrow 4f^{15}$).

1. **Introduction.** — Some of the rare earth ions are stable in more than one valence state. Ce appears in some metallic compounds as Ce$^{3+}$ and in some as Ce$^{4+}$, Sm, Eu, Tm and Yb are divalent in some compounds and trivalent in others. Valence changes of rare earth ions can be brought about in some materials by applying pressure on them [1]. This has been observed, for example, in Ce metal [2], the Sm monochalcogenides [3], TmTe and YbTe [4]. In some rare earth metallic compounds, apparently, the two valence states are energetically very close; the separation between the two 4f configurations is ~ kT. In these compounds the two valence states are populated at measuring temperatures. It was suggested recently that fast fluctuations between such two valence states are the source of the demagnetization of rare earth ions in dilute and concentrated alloy systems [5, 6]. Phenomena associated with such fast fluctuations, leading to an intermediate charge state, have been observed, using the Mössbauer effect technique, in a number of Eu and Yb compounds, as described below. Campagna et al. have concluded recently, from measurements performed by X-ray photoemission spectroscopy.

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(XPS), that the energy necessary to make an interconfiguration excitation through the emission of one f electron into the conduction band is \( \sim kT \) in TmTe, TmSe [7], Sm\textsubscript{2}Gd\textsubscript{1-x}S and Sm\textsubscript{3}Tb\textsubscript{1-x}S [8]. With the XPS method one observes the instantaneous picture of the ions in the two valence states, since the photo excitation takes place in a time short compared to the fluctuation times. Instead of observing therefore an intermediate charge state, as seen in the Mössbauer effect, one observes the two valence states separately.

Charge fluctuation effects may be expected in a system of rare earth compounds (all having the same crystal structure), which is characterized by the fact that a certain rare earth ion is divalent in some of the compounds belonging to the system, and trivalent in the others. For such a system the dimensions of the unit cell of the divalent compounds are always larger than those of the trivalent compounds (for example, in the EuM\textsubscript{2} compounds, having the MgCu\textsubscript{2} structure, the Eu ions are divalent in EuAl\textsubscript{2} with \( a = 8.11 \) Å and in EuP\textsubscript{2} with \( a = 7.73 \) Å and trivalent in Eu in SmFe\textsubscript{2} with \( a = 7.40 \) Å). In compounds of the system having intermediate unit cells, phenomena associated with non unique charge states of the respective rare earth ion may be expected. Following the above mentioned criterion, a number of compounds were investigated and indeed phenomena associated with nonunique charge states were observed in them.

Charge states can easily be identified by the Mössbauer effect in Eu compounds, where the isomer shifts are very sensitive to the charge state of the Eu ions. Divalent Eu compounds have an isomer shift between \(-8.7\) and \(-14.5\) mm/s relative to Eu\textsubscript{2}O\textsubscript{3}. Trivalent Eu compounds have an isomer shift between \(-1.0\) and \(+3.6\) mm/s relative to Eu\textsubscript{2}O\textsubscript{3}. No metallic compounds were found with an isomer shift in the intermediate region between \(-1\) and \(-9\) mm/s [9, 10]. Recoilless absorption studies of the 21.6 keV gamma ray of \(^{151}\)Eu in some intermetallic compounds of Eu, chosen according to the above mentioned criterion, showed strongly temperature dependent isomer shifts, in a region corresponding neither to divalent nor to trivalent Eu ions. The results obtained in these studies were interpreted in terms of fast fluctuations \((\tau < 4 \times 10^{-11} \text{ s})\) of an electron, between a localized 4f level and the conduction band, leading to a fluctuating charge density at the Eu nuclei.

The identification of charge states of Yb cannot be done by isomer shift measurements — as the shifts observed in recoilless absorption measurements of Yb gamma rays, are very small. On the other hand, the magnetic properties of Yb in the two valence states are very different. The ionic ground state of Yb\textsuperscript{2+} (4f\textsuperscript{14}) is \( ^{1}S_0 \) which is diamagnetic. The ionic magnetic moment and the hyperfine fields are all zero for this state. The ionic ground state of Yb\textsuperscript{3+} (4f\textsuperscript{13}) is \( ^{2}F_{7/2} \). Its free ion magnetic moment is \( 4 \mu_B \). The hyperfine magnetic fields acting on the Yb nuclei in magnetic compounds when the Yb ions are divalent will therefore be very different from the fields acting on the Yb nuclei when the Yb ions are trivalent. The measurement of these fields by the Mössbauer effect may reveal the existence of intermediate charge states in some compounds, as was found indeed to be the case for Yb in TmHo\textsubscript{1-x}Fe\textsubscript{2} with \( 0.1 \leq x \leq 0.6 \) and will be described below.

In Sm compounds, identification of the charge states can be done by isomer shift measurements of the 22 keV gamma ray transition in \(^{149}\)Sm [11], but the sensitivity of these measurements is much smaller than for Eu compounds. Ce compounds are not yet open to Mössbauer studies.

Most of the measurements reported here were performed on Eu intermetallic compounds.

2. The theoretical model. — The occurrence of fluctuating charge states of rare earth ions in a metallic compound can be explained by assuming that the energy \( E_{\text{exc}} \) necessary to make an interconfiguration excitation from the 4f\textsuperscript{m-1} configuration to the 4f\textsuperscript{m} configuration, by removing an electron from the conduction band at the Fermi energy \( E_F \), and placing it in the localized 4f level, is small. Fast fluctuations between the two configurations may then take place. \( E_{\text{exc}} \) may have a certain width and may be temperature dependent.

One may express \( E_{\text{exc}} \) as the difference in energy between a localized 4f level at energy \( E_{\text{eff}} \) and the Fermi level [1]. According to this picture, one may look upon the fluctuations as taking place between a localized 4f level of finite width \( \Delta \), located at \( E_{\text{exc}} = E_{\text{eff}} - E_F \) above or below the Fermi level, and the conduction band. The fluctuation time \( \tau \) will, presumably, define the width \( \Delta \) of the localized level. The probability of the fluctuating electron to be in the conduction band will depend on the value of \( E_{\text{exc}} \), the temperature and the multiplicity of the respective ionic states [6]. Thus for Eu, the probability of the fluctuating electron to be in the conduction band and to produce a Eu\textsuperscript{3+} (4f\textsuperscript{6}) configuration, will be given by:

\[
p_3(T, E_{\text{exc}}) = \left\{ 1 + 8[1 + 3 \exp(-480/T) + 5 \exp(-1330/T)]^{-1} \exp(-E_{\text{exc}}/kT) \right\}^{-1} .
\]

This formula is based on the fact that the multiplicity of the Eu\textsuperscript{2+} ground state \((J = 7/2)\) is 8, the ground state of Eu\textsuperscript{3+} is a singlet, the multiplicity of the first excited state of Eu\textsuperscript{3+} \((J = 1)\) is 3 and it lies \( \sim 480 \) K above the Eu\textsuperscript{2+} ground state and the multiplicity of the second excited state of Eu\textsuperscript{3+} \((J = 2)\) is 5 and it lies \( \sim 1330 \) K above the Eu\textsuperscript{2+} ground state.

The probability \( p_3(T, E_{\text{exc}}) \) can be determined experimentally from the position of the absorption line in the recoilless absorption spectrum of the 21.6 keV gamma ray of \(^{151}\)Eu in the compound in which charge fluctuations take place. If \( S_2 \) and \( S_3 \) are the isomer shifts corresponding to pure Eu\textsuperscript{2+} and Eu\textsuperscript{3+} states, respectively, and \( p_3(T, E_{\text{exc}}) = 1 - p_3(T, E_{\text{exc}}) \) is the probability of the electron to be in the localized state and thus produce the Eu\textsuperscript{2+} configuration, then the measured
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Isomer shift $S$ will be given, in the fast fluctuation limit, by:

$$ S = p_2 S_2 + p_3 S_3. \quad (2) $$

The probability $p_3$ is derived, therefore, from the experimental value of $S$, using the relation:

$$ p_3 = \frac{S - S_2}{S_3 - S_2}. \quad (3) $$

Once this probability is determined from the measured isomer shift at a certain temperature, $E_{\text{exc}}$ can be determined from eq. (1).

The fluctuation time $\tau$ can be deduced from the measured line width. The width of the absorption line $\Gamma$ is given for short fluctuation times by:

$$ \Gamma = \Gamma_0 + \pi S_2 - S_3)^2 \tau \left[1 - (p_2 - p_3)^2 \right] \quad (4) $$

where $\Gamma_0$ is the line width in the absence of fluctuation phenomena ($\Gamma, \Gamma_0, S_2$ and $S_3$ are expressed here in units of $s^{-1}$). Formula (4) can be derived from the general equations describing dynamic phenomena in Mössbauer spectra [12, 13].

If $E_{\text{exc}}$ has a spread in energy of $A$ (or in other words, if the $4f$ localized level has a finite energy width $A$), and it is assumed that this spread has a Lorentzian distribution of the form:

$$ D(E) = \frac{\Delta/\pi}{A^2 + (E - E_{\text{exc}})^2} \quad (5) $$

then the expected Mössbauer spectrum will be given by:

$$ I(\omega) = \int_{-\infty}^{+\infty} D(E) \frac{\Gamma/\pi}{\Gamma_0^2 + (\omega - S(T, E))^2} dE \quad (6) $$

where $\Gamma$ is the half width of the Mössbauer absorption line, $I(\omega)$ depends on $E_{\text{exc}}, \Delta, S_2$ and $S_3$.

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:

$$ I_0(\omega) = \frac{(\Gamma/\pi)}{\Gamma_0^2 + (\omega - S_3)^2} + \frac{(\Gamma/\pi)}{\Gamma_0^2 + (\omega - S_2)^2}. \quad (7) $$

It is clear from eq. (7) 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. If $E_{\text{exc}} > \Delta$ the intensity of the Eu$^{2+}$ line relative to the Eu$^{3+}$ line is given by

$$ \frac{I_0(2^+)}{I_0(3^+)} = \frac{\Delta}{\pi E_{\text{exc}}}. \quad (8) $$

In Yb, as mentioned above, the identification of the charge states cannot be done by isomer shift measurements, but by the magnetic properties of the $4f^{14}$ and $4f^{13}$ configurations. Fluctuating charge states will lead in this case to a fluctuating spin density and hyperfine field at the Yb site in a magnetic compound. If the Yb ions in such a compound were divalent, only a small magnetic hyperfine field would act on the Yb nuclei, and the quadrupole interaction in a cubic compound would be zero. (The small field on the Yb nuclei in the diamagnetic Yb$^{2+}$ ion would stem from the conduction electron polarization.) This would result in a somewhat broadened line around zero velocity in the Mössbauer spectrum. If the Yb ions were trivalent, the ionic ground state of Yb$^{3+}$ ($2F_{7/2}$) would be split by the exchange and crystalline fields. A large magnetic hyperfine field and a large electric field gradient would act on the $170Yb$ nuclei at $4.1$ K, and a five line Mössbauer spectrum would be observed. At higher temperatures the magnetic and quadrupole splittings would be determined by the population of the excited levels of the $2F_{7/2}$ state.

If $E_{\text{exc}}$, the energy difference between the lowest state of the $4f^{13}$ configuration and the $4f^{14}$ configuration is of the order of $kT$, then the $4f^{14}$ configuration will be populated together with the various levels belonging to the Yb$^{3+}$, $2F_{7/2}$, ionic ground state, and the fast fluctuations between all the states, will determine the magnetic hyperfine fields and the electric field gradients acting on the Yb nuclei.

The field will be given therefore by

$$ H_{\text{eff}} = \sum_{i=1}^{n} h_i e^{-E_i/kT} \quad (9) $$

where $h_i$ are the energies of the various sublevels of the $2F_{7/2}$ ground state, and $H_{\text{eff}}$ the hyperfine fields corresponding to each of these levels. In the same way the electric field gradient will be given by

$$ q_{\text{eff}} = \sum_{i=1}^{n} q_i e^{-E_i/kT} \quad (10) $$

where $q_i$ are the effective field gradients pertaining to the various levels. $E_{\text{exc}}$ may again have a certain width $\Delta$. In such a case the hyperfine fields and electric field gradients acting on the Yb nuclei will not be unique. If it is assumed that $E_{\text{exc}}$ has a distribution $D(E)$ as given by eq. (5), the recoilless absorption spectra will be given by

$$ I(\omega) = \int_{-\infty}^{+\infty} D(E) S \psi(\omega, E) dE \quad (11) $$

where $S \psi(\omega, E)$ is the Mössbauer spectrum corresponding to $E_{\text{exc}} = E$. $I(\omega)$ is a function of the average values of $E_{\text{exc}}, \Delta, T, H_{\text{eff}}$, and the crystalline field parameters. In this case one may expect at $T = 0$ a superposition of
2 spectra, composed of one line at zero velocity corresponding to the Yb$^{2+}$ configuration and a split spectrum corresponding to a Yb$^{3+}$ configuration.

3. Results of $^{151}$Eu Measurements. — 3.1 Experimental Details. — The source used in all the measurements on Eu compounds was $^{151}$SmF$_3$ at room temperature. The intermetallic compounds investigated, which served as absorbers, were prepared by melting stoichiometric amounts of the elements in an argon atmosphere using an induction furnace. The samples were annealed for 24 hours at 600 °C. During the measurements the absorbers could be held at any temperature between 4 and 700 K. At low temperatures, the temperature was stabilized to within 0.1 K, at higher temperatures to within 0.3 K.

3.2 EuCu$_2$Si$_2$. — Recoilless absorption measurements were performed on the EuM$_2$Si$_2$ system where M is Fe, Cu, or Ag. The compounds crystallize in the tetragonal ThCr$_2$Si$_2$ structure. In EuFe$_2$Si$_2$ and EuAg$_2$Si$_2$, the Fe and Ag ions occupy the 4(d) sites and the Si ions occupy the 4(e) sites. In EuCu$_2$Si$_2$ the Cu and Si ions are distributed between the 4(d) and 4(e) sites, with the Cu ions preferring the 4(d) positions.

The recoilless absorption measurements on the EuM$_2$Si$_2$ compounds were performed at various temperatures between 4 and 670 K. Some of the experimental spectra obtained are shown in figure 1.

In the EuFe$_2$Si$_2$ measurements, a single absorption line with an isomer shift of $-0.7 \pm 0.1$ mm/s is obtained at all temperatures. Such a shift is typical for trivalent europium compounds. The EuAg$_2$Si$_2$ spectra are magnetically split below 20 K. Above 20 K, single unsplit absorption lines are obtained. The isomer shift of the EuAg$_2$Si$_2$ spectra is $-11.4 \pm 0.1$ mm/s at all temperatures, typical for divalent europium compounds. In the EuCu$_2$Si$_2$ spectra, two absorption lines are seen. The isomer shift of the weaker line (which has a relative intensity of about 20 % and is split at 4.1 K) is $-12.4 \pm 0.2$ mm/s at all temperatures, typical for divalent Eu in a metallic environment. The isomer shift of the intense line is temperature dependent. It changes from $-1.8$ mm/s at 4 K to $-7$ mm/s at 670 K (Fig. 1). These changes in the isomer shift are about 100 times larger than those produced by the temperature-dependent second-order Doppler shift. We believe that the intense line corresponds to Eu ions which have 8 Cu ions as their first nearest neighbors [in the 4(d) positions], whereas the weak line corresponds to Eu ions which have one or more Si ions as their first nearest neighbors. The relative intensity of the weak line decreases with temperature, indicating that the recoil-free fraction corresponding to this line is strongly temperature dependent.

The valency of the Eu ions in the EuM$_2$Si$_2$ compounds depends strongly on the interatomic distances. In EuAg$_2$Si$_2$, in which the smallest Eu-Si distance is relatively large (3.317 Å), the Eu ions are divalent. In EuFe$_2$Si$_2$, where this Eu-Si distance is relatively small (3.073 Å), the Eu ions are trivalent. In EuCu$_2$Si$_2$ this Eu-Si distance (3.124 Å) is intermediate between the corresponding distances in EuFe$_2$Si$_2$ and EuAg$_2$Si$_2$. We interpret the line moving with temperature in the recoilless absorption spectra in EuCu$_2$Si$_2$ according to the model of charge fluctuations outlined above.

From the positions of the absorption lines, the values of $p_1$ and $p_2$ as a function of temperature were determined (eq. (3)). The values of $E_{\text{rec}}(T)$ in EuCu$_2$Si$_2$ were calculated from the values of $p_2(T)$ (eq. (1)).

Using eq. (4), and considering the fact that within the experimental accuracy $\Gamma$ does not change with temperature, an upper limit of $4 \times 10^{-11}$ s is determined for the fluctuation time $\tau$.

The calculations of $E_{\text{rec}}$ depend on the value assumed for $S_2$. For all known divalent intermetallic compounds of Eu, the values of $S_2$ are between $-9$
and $-14$ mm/s. The values obtained for $E_{\text{exc}}$ are plotted in figure 2 as a function of $T$, assuming two different values of $S_2$ ($-11.5$ and $-14$ mm/s). It is seen that for $S_2 = -11.5$ mm/s, the value for $E_{\text{exc}}$ is $0.063 \pm 0.003$ eV (or $735 \pm 35$ K) at all temperatures. For $S_2 = -14$ mm/s, $E_{\text{exc}}$ changes from $0.065$ eV at 180 K to $0.086$ eV at 670 K. The conclusion is, therefore, that the difference in energy between the Eu$^{2+}$ and the Eu$^{3+}$ configurations in EuCu$_2$Si$_2$ is about $0.07$ eV ($\sim 800$ K) in the temperature range between 180 and 670 K.

The isomer shifts of all known trivalent metallic compounds of Eu relative to Eu$_2$O$_3$ lie in the region between $+1$ and $+4$ mm/s. The isomer shift of EuCu$_2$Si$_2$ at 4.1 K is $-1.8$ mm/s. We tend to believe that even at low temperatures the Eu ion in EuCu$_2$Si$_2$ is not in a pure $3^+$ state. Because of the small difference in energy between the Eu$^{2+}$ and Eu$^{3+}$ states, the $2^+$ state is probably slightly mixed into the ground state by various perturbations.

3.3 EuRh$_2$. — The size of the unit cell of EuRh$_2$ is 7.531 Å — smaller than the size of the unit cell of EuPt$_2$, in which the Eu ion is divalent and larger than that of SmFe$_2$, in which the Eu ion is trivalent. Recoilless absorption measurements of the 21.6 keV gamma ray of $^{151}$Eu in EuRh$_2$ were performed at a number of temperatures between 4 and 500 K. Some of the spectra obtained are shown in figure 3. In all of the spectra a single narrow absorption line is seen. In the 4.1 K spectra an additional line, 40 times weaker than the main line is observed at a velocity of $-8.5$ mm/s. One clearly observes a shift of the main line as function of temperature, which is much larger than the second order Doppler shift.

Recoilless absorption measurements of the 21.6 keV gamma ray of $^{151}$Eu were performed also in EuAl$_2$ at 90 K and 300 K. The difference in the isomer shift observed in this case at these two temperatures, $\Delta_0 = 0.12$ mm/s, is very small and may be attributed solely to the second order Doppler effect [14]. Assuming that the second order Doppler shift is a linear function of $T$ and is the same in EuRh$_2$ and EuAl$_2$, the experimentally measured line positions in EuRh$_2$ were corrected accordingly. The corrected isomer shifts obtained in EuRh$_2$ relative to EuF$_3$ are shown in figure 4. The shift changes from $+2.14$ mm/s at 4 K and 90 K to $+0.45$ mm/s at 500 K. The width of the moving line does not change as a function of temperature. The values of $p_2(T)$, calculated from the position of the absorption line at the different temperatures and assuming $S_2 = -8.8$ mm/s (as in divalent EuM$_2$ compounds) and $S_2 = 2.14$ mm/s (the shift observed at 4.1 K) yield a value of $E_{\text{exc}}$ of 0.086 eV (1 000 K) at 90 K and of 0.12 eV (1 400 K) at 500 K. The fluctuation time of the electron between the localized level and the conduction band is fast and does not cause any appre-
ciable broadening of the absorption line. The upper limit of the fluctuation time is again $4 \times 10^{-11}$ s. This gives a lower limit of the width $\Delta$ of the localized level of $\sim 0.2$ K. From the intensity of the weak line observed at 4.2 K and using eq. (8) one obtains $\Delta \sim 100$ K.

Magnetic susceptibility measurements of EuRh$_2$ were also carried out. The susceptibility was measured between 80 and 500 K by the Faraday technique. The specimen was placed in an inhomogeneous field produced by an electromagnet and the vertical forces were measured with a Chan electrobalance, which is sensitive to 0.1 $\mu$g. The system was calibrated with Hg[Co(SCN)$_2$]. The measurements were performed in a helium atmosphere. The results of the measurements are shown in figure 5.

- The susceptibility of EuRh$_2$. The upper line is the theoretical susceptibility of Eu$^{2+}$, the lower line is the theoretical susceptibility of Eu$^{3+}$. The middle line is the measured susceptibility of EuRh$_2$. The points are the theoretical susceptibilities of EuRh$_2$, calculated as described in the text.

The magnetic properties of the Eu ions in the two valence states are quite different. The ionic ground state of Eu$^{2+}$ (4f$^7$) is $^8S_{7/2}$, the same as that of Gd$^{3+}$. Its free ion magnetic moment is $7 \mu_B$. The ionic ground state of Eu$^{3+}$ (4f$^6$) is $^5F_0$, which is diamagnetic. The ionic magnetic moment and the hyperfine field are zero for this state. The first excited state of Eu$^{2+}$ at $\sim 480$ K is a $J = 1$ state, the second excited ionic state at $\sim 1330$ K is a $J = 2$ state. Both these states carry magnetic moments. The susceptibility of Eu$^{2+}$ was calculated as a function of temperature, by taking into account the mixing of the $J = 1$ and $J = 2$ states into the ground state by the magnetic field and the thermal population of these states [15]. The susceptibility in an intermediate valence state was calculated using the relation:

$$x(T) = p_3(T) x_3(T) + (1 - p_3) x_2(T)$$

where $x_3(T)$ is the susceptibility of a Eu$^{3+}$ ion and $x_2(T)$ the susceptibility of a Eu$^{2+}$ ion.

The upper line in figure 5 is the calculated susceptibility of Eu$^{3+}$, and the lower line is the susceptibility of Eu$^{2+}$. The experimental line falls in between. The theoretical values of the susceptibility of EuRh$_2$ were calculated from eq. (12) taking for $p_3(T)$ the values obtained from the Mössbauer measurements. These are shown as points in the figure and fit well the experimental susceptibility. In obtaining the fit, a value of $\sim 20$ K for $\theta$, the paramagnetic Curie temperature had to be assumed.

3.4 Eu$_{0.125}$La$_{0.875}$Rh$_2$, Eu$_{0.125}$Pr$_{0.875}$Rh$_2$. — The size of the unit cell of LaRh$_2$ is 7.646 Å, and of PrRh$_2$ is 7.575 Å. By preparing ternary Eu$_{1-x}$La$_x$Rh$_2$ or Eu$_{1-x}$Pr$_x$Rh$_2$ compounds, one obtains unit cells which are somewhat larger than the unit cell of EuRh$_2$ ($a = 7.531$ Å). In EuRh$_2$, the 4f localized level lies at about 1,000 K and is not appreciably populated at the measuring temperatures. In Eu$_{1-x}$La$_x$Rh$_2$ compounds, with somewhat larger unit cells, one might expect the 4f localized level to lie closer to the Fermi level, and larger shifts as function of temperature are expected.

Recoilless absorption measurements of the 21.6 keV gamma ray of $^{151}$Eu in 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, 295 and 400 K). 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 figures 6 and 7. The following features characterize the experimental spectra: (a) The spectra are composed of a few lines which correspond to Eu ions having a different number of La neighbors. (b) At very low temperatures (4.1 K) the spectra are composed of 2 lines. One of the lines is at a velocity of $\sim + 2$ mm/s, which is characteristic of Eu$^{3+}$ ions in metallic systems, and the second line is at a velocity of $\sim - 6.5$ mm/s, 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. (c) The isomer shifts of the various absorption lines vary continuously very significantly as a function of temperature.

All the experimental results can be explained by the model of fast fluctuations outlined above if it is assumed that $E_{vee}$ 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
MÖSSBAUER EFFECT STUDIES OF INTERCONFIGURATION FLUCTUATIONS

Fig. 6. — Recoilless absorption spectra of the 21.6 keV gamma ray of $^{151}$Eu in Eu$_{0.125}$La$_{0.875}$Rh$_2$. The solid lines are the theoretical best fits to the experimental spectra.

nearest neighbors in an Eu$_x$La$_{1-x}$Rh$_2$ compound is given by

$$Q_M(x) = \frac{4}{M} x^{4-M} (1-x)^M. \quad (13)$$

For $x = 0.125$, $Q_4 = 0.585$, $Q_3 = 0.335$, $Q_2 = 0.072$, $Q_1 = 0.007$ and $Q_0 = 0.0002$. It is therefore clear that for $x = 0.125$, practically only $Q_4$, $Q_3$ and $Q_2$ have to be taken into account, and it is really found that the Eu$_{0.125}$La$_{0.875}$Rh$_2$ spectra at temperatures above 50 K are composed of 3 lines with intensities given by $Q_4$, $Q_3$ and $Q_2$ (Fig. 6). For $x = 0.25$, the spectra are composed of 4 absorption lines, corresponding to $M = 1, 2, 3, 4$. These lines are shown as dotted curves in figure 7. The spectra of other Eu$_x$La$_{1-x}$Rh$_2$ compounds are composed of several lines with intensities determined by the values of $Q_M(x)$.

The probability of the fluctuating electron to be in the conduction band will be given in this case by eq. (1), with $E_{\text{exc}}$ being a function of $M$, ($E_{\text{exc}}^M$), and thus $p(T)$ will be different for each value of $M$.

In order to get good fits to the experimental spectra, especially to those measured at very low temperatures, we had to assume that $E_{\text{exc}}$ has a certain spread $\Delta E_{\text{exc}}$, which is also a function of $M$, the number of La nearest neighbors. This spread may represent the natural width of the 4f levels or it may be produced by an inhomogeneity caused, for example, by the dependence of $E_{\text{exc}}$ on the number of La second nearest neighbors.

If it is assumed that the spread in $E_{\text{exc}}^M$ has a Lorentzian distribution

$$D_M(E) = \frac{\Delta M/\pi}{\Delta E^2 + (E - E_{\text{exc}}^M)^2} \quad (14)$$

then the expected Mössbauer spectrum will be given by

$$I(\omega) = \sum_{M=0}^{M=4} Q_M(x) \int_{-\infty}^{+\infty} D_M(E) \frac{\Gamma/\pi}{\Gamma^2 + (\omega - S(T, E))^2} \, dE \quad (15)$$

$I(\omega)$ depends, in this case, on ten free parameters: The excitation energies $E_{\text{exc}}^M$ and their widths $\Delta E$ for $M = 0, 1, 2, 3$ and 4. For $x = 0.075$ and $x = 0.125$, practically only the six parameters corresponding to $M = 2, 3$ and 4 have to be taken into account.

Least square computer fits to all the experimental spectra were made using eq. (15). The values of the parameters $E_{\text{exc}}^M$ derived from these fits are summarized in Table I. The values derived for $\Delta E$ varied between 40 and 80 K and the values for $\Delta E$ varied between 60 and 150 K. The values of $\Delta E$ and $\Delta E$ were larger than 200 K. The solid lines in figures 6 and 7 are the theoretical fits to the experimental spectra. The dotted lines in figure 7 correspond to different Eu sites characterized by $M$, the number of La nearest neighbors. The values
Values of $E_{\text{exc}}$ 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 K units)

<table>
<thead>
<tr>
<th>$x$</th>
<th>$T$(K)</th>
<th>$E_{\text{exc}}^0$</th>
<th>$E_{\text{exc}}^1$</th>
<th>$E_{\text{exc}}^2$</th>
<th>$E_{\text{exc}}^3$</th>
<th>$E_{\text{exc}}^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.075</td>
<td>4.1-400</td>
<td>100±40</td>
<td>150±50</td>
<td>100±50</td>
<td>140±50</td>
<td>150±50</td>
</tr>
<tr>
<td>0.125</td>
<td>4.1</td>
<td>20±10</td>
<td>250±50</td>
<td>250±50</td>
<td>300±50</td>
<td>350±50</td>
</tr>
<tr>
<td>0.125</td>
<td>15</td>
<td>30±15</td>
<td>270±100</td>
<td>&gt;1000</td>
<td>&gt;1000</td>
<td></td>
</tr>
<tr>
<td>0.125</td>
<td>55</td>
<td>55±15</td>
<td>270±100</td>
<td>&gt;1000</td>
<td>&gt;1000</td>
<td></td>
</tr>
<tr>
<td>0.125</td>
<td>200±30</td>
<td>550±50</td>
<td>1000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>25</td>
<td>50±20</td>
<td>300±50</td>
<td>350±50</td>
<td>400±50</td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>70</td>
<td>100±30</td>
<td>350±50</td>
<td>400±50</td>
<td>450±50</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>89</td>
<td>75±30</td>
<td>450±50</td>
<td>500±50</td>
<td>550±50</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>100-400</td>
<td>180±40</td>
<td>450±50</td>
<td>550±50</td>
<td>650±50</td>
<td></td>
</tr>
<tr>
<td>Eu$<em>{1/6}$Pr$</em>{7/6}$Rh$_{2}$</td>
<td>80-400</td>
<td>550±40</td>
<td>1000</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.5 EuRh$_{2-x}$Pt$_{x}$ — The size of the unit cell of EuPt$_2$ is 7.731 Å, as mentioned above. In this compound the Eu ions are divalent. In the ternary EuRh$_{1-x}$Pt$_x$ compounds, which also crystallize in the cubic Laves phase MgCu$_2$ structure, the size of the unit cell is intermediate between that of EuRh$_2$ and that of EuPt$_2$ and intermediate charge states of Eu are obtained in these compounds. Recoilless absorption measurements of the 21.6 keV gamma ray of $^{151}$Eu in EuRh$_{2-x}$Pt$_x$ for $x = 0.125, 0.25, 0.5$ and 1 were performed at various temperatures between 4 and 500 K. Most of the spectra obtained at 4.1 K in these compounds are composed of 2 split spectra, one with its center of mass corresponding to the isomer shift of Eu$^{3+}$, the other with its center of mass corresponding to the isomer shift of Eu$^{2+}$ ions. In the spectra of EuRh$_{1.875}$Pr$_{0.125}$, EuRh$_{1.75}$Pt$_{0.25}$ and EuRh$_{1.5}$Pt$_{0.5}$ at 90 K, essentially two unsplit lines are seen, each line corresponding to either Eu$^{3+}$ or Eu$^{2+}$. These spectra are shown in figure 8. The spectra of EuRhPt and EuPt$_2$ are still split at 90 K and are, therefore, shown at higher temperatures. In figure 9 the spectra obtained in EuRh$_{1.5}$Pt$_{0.5}$ at various temperatures are shown. One observes that at higher temperatures the gap between the two main lines is filled and a smeared spectrum is obtained. The spectra of the other EuRh$_{2-x}$Pt$_x$ compounds change similarly as a function of temperature.

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 line width in the absence of fluctuation phenomena. This assumption implies that the characteristic fluctuation time between the 4f localized level and the conduction band is shorter than $4 \times 10^{-11}$ s. Such short fluctuation times are consistent with the values of $\sim 100$ K found for the widths of the localized 4f level. Such a width corresponds to a lifetime of $\sim 10^{-13}$ s.

For $x = 0.5$ for example, $Q_0 = 0.0317$, $Q_1 = 0.127$, $Q_2 = 0.232$, $Q_3 = 0.257$, $Q_4 = 0.193$, $Q_5 = 0.103$, $Q_6 = 0.04$, $Q_7 = 0.011$ and $Q_8 = 0.002$. From the
compounds, which is consistent with all the experimental results is
\[ E_{\text{exc}} = 950 + 1300x + T - 525m. \]  

4. Results of $^{170}$Yb measurements. \( \text{Yb : Tm}_{x}\text{Ho}_{1-x}\text{Fe}_2 \). \( \text{Recoilless absorption studies of the 84 keV gamma ray of }^{170}\text{Yb } \)
emitted from \( \text{Yb : Tm}_{x}\text{Ho}_{1-x}\text{Fe}_2 \) sources, with \( x = 0.1, 0.2, 0.4 \) and 0.6, were performed between 4.1 K and 70 K. The absorber used in these measurements was an enriched $^{170}$Yb metal disc at 4.1 K, which gives a (slightly broadened) single absorption line. The \( \text{Tm}_{x}\text{Ho}_{1-x}\text{Fe}_2 \) compounds were prepared by melting stoichiometric amounts of the elements in an argon atmosphere using an induction furnace. The samples were neutron irradiated to produce the $^{170}$Tm radioactive source, which decays to $^{170}$Yb and emits the 84.3 keV ($2^+ \to 0^+$) gamma ray. The source was annealed for 24 hours at 850°C. This annealing is essential to repair strong radiation damage. The sources were inserted in small lucite ovens \( \text{[17]} \), the \( \text{V~ELocity (mm/s)} \) of which could be changed between 4.1 K and 75 K.

Some of the experimental spectra obtained are shown in figure 10. All the spectra are composed of two sub-spectra, one of which is a five line split spectrum and the other a broadened line at zero velocity. The spectra can be explained by the charge fluctuation model.
outlined above, if it is assumed that $E_{\text{exc}} \sim 150$ K and $A \sim 120$ K.

$\text{Tm}_2\text{Ho}_{1-x}\text{Fe}_2$ also fulfills the criterion for the size of the unit cell mentioned above: In most Laves phase $\text{YbM}_2$ compounds, Yb is divalent. Yb in $\text{TmFe}_2$ (used as source) is trivalent. The size of the unit cell of $\text{YbRh}_2$, for example, in which the Yb ion is divalent, is $7.432$ Å. The size of the unit cell of $\text{TmFe}_2$ is $7.247$, and that of $\text{HoFe}_2$ is $7.287$ Å. Thus, by mixing Tm with Ho in $\text{Tm}_2\text{Ho}_{1-x}\text{Fe}_2$, the unit cell is somewhat larger than in $\text{TmFe}_2$, and mixed charge states are obtained in this compound.

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References