and 6.0 eV, again with differences in the respective profiles attributed to matrix elements. According to Fig. 3(b), process 1 appears to contribute the high-energy part of the 7.71 eV, extending from $E = 8.0$ to 10.2 eV. Note the two features centered at $E = 8.5$ and 9.6 eV, respectively. The latter is not described in Fig. 3(b) since the band structure actually used extends up to $E = 9$ eV only. This peak gives evidence for additional states distributed at $E > 9.0$ eV, i.e., just above the d band. They are populated here up to $E \simeq 10.2$ eV through process 1, initiating at $E \simeq -1.7$ eV via states lying at $E \simeq 2.5$ eV. If this level delineates the high-energy edge of p_3, the upper limit of process 2 contribution to the spectrum should be located at $E = 10.2 - 4.16 \simeq 6.0$ eV, which is quite precisely observed [Fig. 3(b)]. The upper limit of the 3.51-eV spectrum is around $E = 6.1$ eV which corresponds (via process 1) to a p_3 level at $E = 6.1 - 3.51 \simeq 2.6$ eV, in agreement with the 7.71-eV spectrum. This sets for the first time the upper edge of p_3, in close agreement with calculations.

Altogether, the present experiment confirms the band structure of Maschke.[6] It brings unique information on the width of p_3 and the upper-lying conduction-band states. Worth noting is the fact that the above experimental data are *not sensitive* to surface aging, i.e., information therein obtained is characteristic of the bulk electronic structure.

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X-Ray Photoelectron Spectroscopy of the Intermediate-Valence State in the $EuRh_{2-x}Pt_x$ System

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By considering the results of Mössbauer studies and x-ray photoelectron spectroscopy, we obtain a phenomenological model of the intermediate valence state in the homogeneous system $EuRh_2$. The interconfiguration excitation energy is 1550 ± 150 K, and the mixing width, 2Δ, is 0.10 ± 0.02 eV. In $EuRh_{2-x}Pt_x$ the Eu valence is determined by the local environment, including neighbors beyond the nearest shell.

The intermediate valence phenomenon[1] has most often been investigated by measurement of static (adiabatic) parameters, e.g., the unit cell, conductivity, thermal properties, susceptibility, and Mössbauer spectra. However, only measurements in the sudden or high-frequency limit can reveal the electronic configuration involved in the fluctuations. This distinction has often been related to the "measuring time" of the technique compared to the fluctuation time[2] τ_f of the system. In this picture the time scale of Mössbauer spectroscopy is set by nuclear lifetime and hyperfine frequencies, typically 10^{-11} sec, which, as we shall show, are long enough so that only an average state is observed. It is generally recognized that the measuring time in x-ray photoelectron spectroscopy (XPS) is of the order of 10^{-17} sec. However, it introduces a large perturbation by the removal of one electron. Nevertheless it is of great interest to study by XPS systems which have been found by other techniques to be in an intermediate valence state. Such studies have been conducted with systems containing Sm and Tm ions.[3] SmB_6 has been studied by the Mössbauer technique,[4,5] showing definitely an isomer shift which lies between that of

Sm^{2+} and Sm^{3+}. Mössbauer studies of SmS in the collapsed phase[5] indicate that $\tau_f < 10^{-9}$ sec. Mössbauer studies of the Eu mixed valence systems have shown that $\tau_f < 10^{-11}$ sec.[6,7] Here we present the first XPS study of an intermediate valence system with Eu, $EuRh_{2-x}Pt_x$, one previously studied by susceptibility, x-ray and Mössbauer effect.[7] The results obtained from the XPS spectra concerning the amounts of Eu^{2+} and Eu^{3+} in these systems combined with the Mössbauer observations lead to a clear phenomenological picture of the intermediate valence phenomenon in $EuRh_2$ as well as in the $EuRh_{2-x}Pt_x$ system. In $EuRh_2$, all observations are consistent with an interconfiguration excitation energy E_{exc} of 1550 ± 150 K and with a total mixing width, $2\Delta = \hbar/\tau_f$, of 1250 ± 200 K (0.1 eV) corresponding to a "fluctuation time," τ_f, of $(0.6 \pm 0.1)\times 10^{-14}$ sec. This is the first experimental determination of this important physical quantity.

The samples of $EuRh_2$, $EuRh_{1.5}Pt_{0.5}$, and $EuPt_2$ were those previously studied by the Mössbauer effect.[6,7] The XPS measurements were performed in a HP 5950*A* electron spectroscopy for chemical analysis spectrometer. The sample surfaces were scraped inside the machine (in 3×10^{-9} Torr) before the measurement. Spectra of the 4*d* electron region are shown in Fig. 1. Spectra taken a few hours after the scraping show an appreciable buildup of an oxide layer.

In Fig. 1, curve *A*, we display the experimental 4*d*-electron emission spectrum of $EuPt_2$. Since we know from all our previous studies that the Eu ion is divalent in $EuPt_2$ (a pure divalent line in Mössbauer spectroscopy, ferromagnetic with $T_c \sim 105$ K), the extra additional Eu^{3+} emission lines were assumed to belong to an oxide layer. After exposing the $EuPt_2$ sample for 10 min to air at 80°C, the spectrum obtained was that shown in Fig. 1, curve *A*1. The spectrum of this fully oxidized $EuPt_2$ surface is indeed at the energy of the "extra" Eu^{3+} lines in Fig. 1, curve *A*. After subtracting a suitable amount of the oxide component from the $EuPt_2$ experimental spectrum, we obtain the spectrum shown in Fig. 1, curve *A*2 which is a typical Eu^{2+} metallic 4*d* x-ray photoelectron spectrum, even including a suggestion of the fine features of the 4*f* multiplet structure on the 4*d* line.[8] The experimental spectrum of $EuRh_2$ (Fig. 1, curve *B*) is composed of a main trivalent component and a weaker divalent component, shown in Fig. 1, *B*1 (obtained from Fig. 1, *A*2). After subtraction of the divalent component, the residual Eu^{3+} spectrum is indeed a *metallic* Eu^{3+} ($^7F_0$) spectrum, differing very much from the *oxide* spectrum (shifted by 1.2 eV and with much narrower emission lines). The spectrum is very similar to that observed for Sm^{2+} in SmTe.[9]

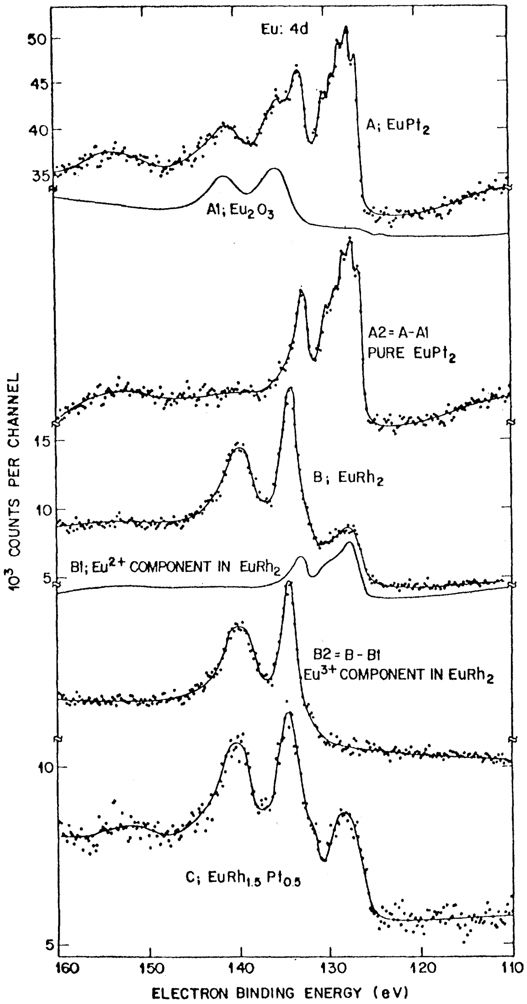

FIG. 1. Curves *A*, *B*, and *C* represent the experimentally observed Eu 4*d* photoelectron spectra at 300 K from $EuPt_2$, $EuRh_2$, and $EuRh_{1.5}Pt_5$, respectively. Curve *A*1 is the 4*d* spectrum of Eu in Eu_2O_3; *A*2 was obtained by *A* − *A*1, *B*1 by reducing *A*2, and *B*2 by the subtraction *B* − *B*1.

The relative areas of the Eu^{3+} and Eu^{2+} components in Fig. 1, curves *B* and *C*, show that in pure $EuRh_2$ the fraction of divalent component, p_2(300 K) is 0.20 ± 0.05, while in $EuRh_{1.5}Pt_{0.5}$ it is 0.40 ± 0.10. These results are in excellent agreement with what one could expect from the general systematics of the unit-cell sizes of these samples. This is most clearly visible in Fig. 2 of Ref. 7.

Within the language of a "measuring time" the Mössbauer and XPS studies of the homogeneous system $EuRh_2$ prove beyond reasonable doubt that the charge fluctuation time is short compared to the relevant Mössbauer time ($\sim 10^{-11}$ sec) and long relative to the relevant XPS time ($\sim 10^{-17}$ sec), yielding a single line corresponding to an average isomer shift (or valence) in the Mössbauer case and a superposition of two spectra in the XPS case. However, one can take a further step and use the XPS result of $p_2(300\text{ K}) = 0.20 \pm 0.05$ to obtain a full understanding of the observed temperature dependence of the isomer shift, and derive the interconfiguration excitation energy and the charge fluctuation time.

The temperature dependence of the isomer shift measured by the Mössbauer effect in a mixed valence state is expressed by

$$S(T) = S_3 p_3(T) + S_2 p_2(T) = (S_2 - S_3) p_2(T) + S_3 . \quad (1)$$

Here S_2 and S_3 are the isomer shifts for pure divalent and trivalent states in the system. Since in $EuRh_2$ both Eu^{2+} nuclei are exposed to the same conduction-electron charge density, the value of $S_2 - S_3$ should be the same as in insulators, namely, -13 ± 1 mm/sec. Since the isomer shift at 300 K is 1.2 mm/sec, we obtain for S_3 the value 3.8 ± 0.4 mm/sec, comparable to the value obtained for purely metallic Eu^{3+} in $EuPd_3$.[10] We obtain from $S(4.2\text{ K}) = 2.2$ mm/sec that at absolute zero $p_2(0\text{ K}) = 0.12 \pm 0.03$, i.e., even at 0 K the Eu ion is in an intermediate valence state in $EuRh_2$. One can now try to reconstruct the temperature dependence of the isomer shift within the simple model presented in Ref. 6. Within this model, a $4f$ localized state of width 2Δ (full width at half-maximum) exists at an energy E_{exc} above the Fermi level (Fig. 2). Assuming a Lorentzian energy distribution, $p_2(0\text{ K})$ should equal $\pi^{-1}\arctan(\Delta/E_{\text{exc}})$. At finite temperature the probability of the Eu ion being divalent is given by[6]

$$p_2(T) = \int_{-\infty}^{\infty} \frac{\Delta/\pi}{\Delta^2 + (E - E_{\text{exc}})^2} \times \frac{dE}{1 + (Z_3/8)\exp(E/kT)} , \quad (2)$$

where

$$Z_3 = 1 + 3\exp(-480/T) + 5\exp(-1330/T) + 7\exp(-2600/T) \quad (3)$$

is the single-ion J multiplet partition function of Eu^{3+}. Since Δ must equal $E_{\text{exc}}\tan[\pi p_2(0\text{ K})]$, Eqs. (1)–(3) define the curve of $S(T)$ with only one free parameter: E_{exc}. With $E_{\text{exc}} = 1550$ K, we obtain the theoretical curve shown in Fig. 3. This leads to $\Delta = 625$ K and $\tau_f = (0.6 \pm 0.1) \times 10^{-14}$ sec. The width of the $4f$ localized "virtual" level is 0.1 eV, consistent with theoretical expectations. In the above derivation it was assumed that E_{exc} is temperature-independent. One may allow a linear decrease of E_{exc} with temperature and obtain even better agreement between theory and experiment. However, in the case of $EuRh_2$, unlike in $EuCu_2Si_2$,[6,11] the temperature dependence of E_{exc} is relatively weak.

The Mössbauer spectra of $EuRh_{2-x}$ at 4.2 K show both divalent and trivalent components. The

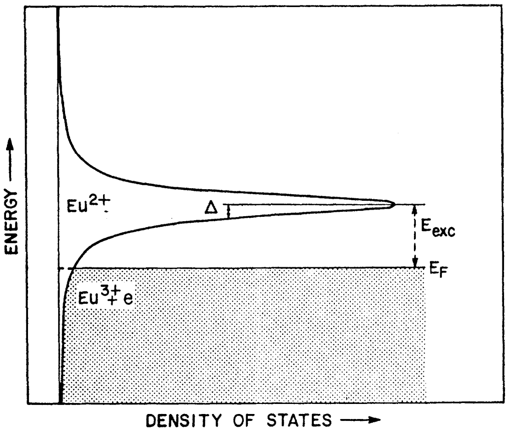

FIG. 2. Schematic representations of a localized $4f$ level with width at half-height 2Δ, at an energy E_{exc} above the Fermi level.

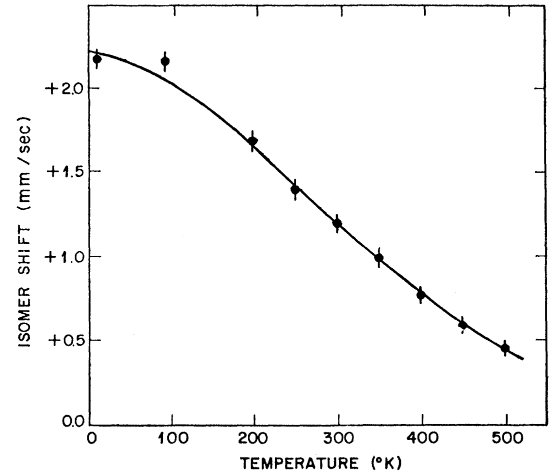

FIG. 3. The temperature dependence of the isomer shift in $EuRh_2$. The solid curve is a theoretical curve from Eqs. (1)–(3), obtained by adjusting the single parameter E_{exc} to 1550 K.

ratio of intensities does not correspond to a division according to the statistical distribution of nearest neighbors. This led Bauminger *et al.*[6] to the phenomenological picture of a wide $4f$ level with both natural (homogeneous) and inhomogeneous broadening, which intersects the Fermi level and thus contributes to a pure divalent component even at 0 K. Since a natural broad level implies fast charge fluctuations (so that only an average line should be observed), we conclude that in the case of EuRh$_{2-x}$Pt$_x$ the width of the $4f$ level is an inhomogeneous width due to second- and further-neighbor effects which determine whether the Eu will be divalent or trivalent.

In conclusion we point out that XPS studies of Eu intermediate valence systems combined with other techniques, in particular the Mössbauer effect, may clarify many details of the mixed-valence phenomenon. In the case of EuRh$_2$, a single number [p_2(300 K)] obtained from the XPS spectrum was sufficient to lead to the deduction of the interconfiguration excitation energy and the charge fluctuation time $(0.6 \pm 0.1) \times 10^{-14}$ sec, which agrees with all theoretical expectations and recent neutron-diffraction results.[12]

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New Principle for the Determination of Potential Distributions in Dielectrics

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In this paper we describe the principles of a new, nondestructive method of determination of the potential distribution in delectrics. It is shown that a pressure discontinuity propagated in a sample acts as a virtual probe sensitive to potentials. The time dependence of such externally measurable parameters as voltages or charges on the electrodes is thus a direct image of the inner potential distribution which existed in the sample before the introduction of the perturbation.

During the last few years many efforts have been devoted to the determination of charge, potential, or field distributions in condensed matter. In a plasma or in a liquid, such a determination can be easily done using moving probes. In solids, this information, which can be highly valuable in the analysis of the polarization processes, space-charge build up, and transport phenomena, is so far obtainable in some limited cases only: either by the combination of standard surface-charge measurements and thermally stimulated currents,[1-3] or by successive surface-charge measurements or progressively thinned samples[4,5] or by spectroscopic methods.[6] These