Pressure-Induced Valence Change of Eu in $Eu(Pd_{0.8}Au_{0.2})_2Si_2$: Collapse of Magnetic Order

M. M. Abd-Elmeguid,[a] Ch. Sauer, and W. Zinn
Institut für Festkörperforschung, Kernforschungsanlage Jülich, D-5170 Jülich, West Germany

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We report the first observation of a pressure-induced breakdown of a magnetically ordering Eu^{2+} $(J=\frac{7}{2})$ state to a nonmagnetic intermediate-valent state in antiferromagnetically ordered $Eu(Pd_{0.8}Au_{0.2})_2Si_2$. The experimental results allow us to determine the limits of the range of the Eu mean valence of $2.0 \leqslant \bar{v} \leqslant 2.2$ at 4.2 K, over which magnetic order and intermediate valence can coexist.

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A central issue connected with the phenomenon of intermediate valence (IV) is the question of whether an IV $4f$ system may order magnetically or not.[1] By a valence transition (e.g., $Eu^{2+} \rightarrow Eu^{3+}$) the Eu ion is transferred from a divalent magnetic $(4f^7\,{}^8S_{7/2}$, $\mu = 7\mu_B)$ state into a trivalent nonmagnetic $(4f^6\,{}^7F_0$, $\mu = 0)$ state. As a consequence, any magnetic order (MO) which may exist in the divalent region will be finally destroyed when the trivalent region is reached. Up to now, no Eu compound is known which shows *clear evidence* for the simultaneous existence of MO and IV. Promising progress has been achieved by Segre *et al.*[2] and Gupta *et al.*[3] by investigating the $ThCr_2Si_2$-type structure series $Eu(Pd_{1-x}Au_x)_2Si_2$ $(0 \leqslant x \leqslant 0.25)$ using the ^{151}Eu Mössbauer effect (ME), magnetic susceptibility (χ), and L_{III}-x-ray absorption techniques. Combining the homogeneous IV compound $EuPd_2Si_2$ with the homogeneous MO (antiferromagnetic) compound $EuAu_2Si_2$, the authors suggested a "global" phase diagram: a nonmagnetic region with a first-order IV transition $(Eu^{2+} \rightarrow Eu^{3+})$ for $x < 0.175$ and a MO (antiferromagnetic) region for $0.175 < x \leqslant 0.25$. It was supposed further that in the range $0.175 < x \leqslant 0.25$, MO and a weak IV behavior may coexist. However, this last conclusion was based on L_{III}-x-ray absorption measurements. This method has been very recently contested by Sampathkumaran *et al.*[4] for its suitability in determing the valence of Eu in $EuPd_2P_2$. On the other hand, ME spectroscopy is not controversial for the determination of valence changes, although there are some problems with respect to the evaluation of the absolute valence.

In the present work on the system $Eu(Pd_{1-x}Au_x)_2Si_2$, we demonstrate a new possibility for studying the competition between MO and IV within *one system,* namely by a well-defined decrease of the lattice parameter (high pressure), preserving the chemical composition. Since the unit-cell volume of the series decreases on reduction of the Au concentration (Pd is smaller than Au), two divalent antiferromagnetically ordering compounds [$EuAu_2Si_2$ and $Eu(Pd_{0.8}Au_{0.2})_2Si_2$] have been selected as high-pressure (hp) candidates. The former sample $(x=1)$ is far away from the critical concentration of $x=0.175$ for the phase boundary between MO and IV, whereas the second sample $(x=0.2)$ is located very close. With the ^{151}Eu hp-ME technique, it should be possible to drive both samples from the MO state towards the IV state. The ME method allows us to inspect "simultaneously" the pressure-induced changes of both the Eu mean valence (via the ^{151}Eu ME isomer shift S) and the magnetic order of the Eu ions [via the effective magnetic hyperfine (hf) field B_{eff}]. It will be shown that $EuAu_2Si_2$ behaves under pressure as a stable Eu^{2+} intermetallic compound, whereas $Eu(Pd_{0.8}Au_{0.2})_2Si_2$ displays a distinct valence change towards Eu^{3+} at 300 and 4.2 K. The pressure-induced valence change at 4.2 K is accompanied by a collapse of the magnetic hf field. This is the first observation of a pressure-induced breakdown of the magnetically ordered Eu^{2+} state to the nonmagnetic IV state. Correlating the pressure-induced changes of both S and B_{eff}, it is possible to obtain the range of coexistence between MO and IV in this compound. The experimental results allow us further to conclude that the breakdown of the MO under pressure is primarily caused by the suppression of the ordering temperature rather than of the magnetic moment.

The investigated samples were synthesized as described in the literature.[2] The phase purity of the $ThCr_2Si_2$ structure and the lattice parameter have been proven by x-ray diffraction at room temperature. The χ measurements (4.2–250 K) were carried out with a sensitive Faraday magnetometer equipped with superconducting magnets. The ME measurements ($^{151}Sm_2O_3$ source) were performed at various temperatures between 1.3 and 300 K and at pressures up to 54 kbar (300, 77, and 4.2 K) by means of a hp setup described elsewhere.[5] An external field (10 T) has been applied to determine the sign of B_{eff} in both samples.

The χ data show that $EuAu_2Si_2$ and $Eu(Pd_{0.8}Au_{0.2})_2Si_2$ order antiferromagnetically ($T_N = 6.5$ and 32 K, respectively) and exhibit Curie-Weiss behavior above the Néel temperature. The effective magnetic moment per Eu atom ($\mu_{\text{eff}} = 8.1\mu_B$ and

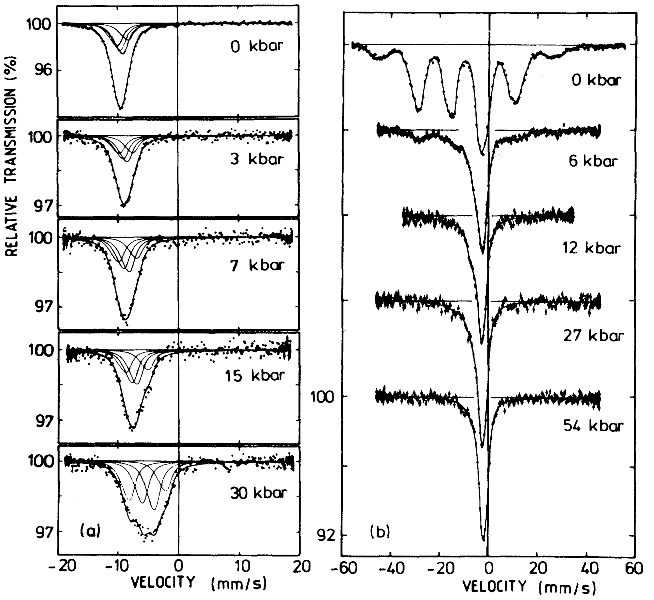

FIG. 1. Typical ^{151}Eu-Mössbauer spectra of Eu(Pd$_{0.8}$Au$_{0.2}$)$_2$Si$_2$ at (a) $T=300$ K and (b) $T=4.2$ K at various pressures.

7.92μ_B, respectively) is found to be very close to that of a free Eu^{2+} ion ($\mu_{eff}=7.94\mu_B$). Also, the temperature dependence of B_{eff} (negative sign in both samples) as deduced from the ME measurements at ambient pressure can be well described by a Brillouin function with $S=\frac{7}{2}$. Furthermore, the temperature-induced change of the isomer shift ($\partial S/\partial T$) at $p=0$ kbar [see Fig. 2(a)] turned out to be very weak and of negative sign [$(-2\pm1.5)\times10^{-4}$ and $(-9\pm2)\times10^{-4}$ mm/s·K for EuAu$_2$Si$_2$ and Eu(Pd$_{0.8}$Au$_{0.2}$)$_2$Si$_2$, respectively]. The negative sign indicates that the electron density at the Eu nucleus decreases with increasing temperature, which is caused by the thermal lattice expansion rather than by a thermal admixture of the Eu^{3+} configuration to the Eu^{2+} ground state. From combination of all above results at ambient pressure, it can be concluded that in both samples the Eu ion is in a pure divalent $4f^7$ (Eu^{2+}) ground state.

Figure 1(a) shows some typical ME spectra for Eu(Pd$_{0.8}$Au$_{0.2}$)$_2$Si$_2$ at 300 K and at different pressures. These spectra could be fitted fairly well by a superposition of Lorentzian lines corresponding to different Pd/Au neighbor (nn) configurations around the Eu ions. At 4.2 K [Fig. 1(b)] the sample displays ($p=0$ kbar) a magnetic hf splitting which indicates MO below the Néel temperature ($T_N=32$ K). These spectra were similarly fitted by a superposition of 3–4 different magnetically split subspectra with different values of B_{eff} and S. In all cases (300 and 4.2 K at $p=0$ kbar), the relative areas of the subspectra obtained by the fit were in good agreement with that expected from the binomial distribution for $x=0.2$. On this basis one can evaluate average values $\bar{S}$ and $\bar{B}_{eff}$. As shown in Fig. 1(a), the ME spectrum displays a sizable shift of $\bar{S}$ towards positive velocities (Eu^{3+}) with increasing pressure. The observed line broadening reflects the individual response to high pressure of the Eu ions exposed to different local environments. The results of the pressure dependence of the isomer shift at 300 K are plotted in Fig. 2(b). Similar to stable Eu^{2+} intermetallic compounds, the pressure-induced change of S in EuAu$_2$Si$_2$ is found to be relatively small, $\partial S/\partial p=(+2.8\pm0.2)\times10^{-2}$ mm/s·kbar or $\partial S/\partial \ln V=-31$ mm/s with an average value for Eu^{2+} intermetallic compounds of the compressibility of $\kappa\simeq0.9\times10^{-3}$ kbar^{-1}. For Eu(Pd$_{0.8}$Au$_{0.2}$)$_2$Si$_2$, we obtain a value of $\partial\bar{S}/\partial p=(+14\pm1)\times10^{-2}$ mm/s·kbar or $\partial\bar{S}/\partial \ln V=-115$ mm/s, which is five times larger than that for EuAu$_2$Si$_2$ and even twice that

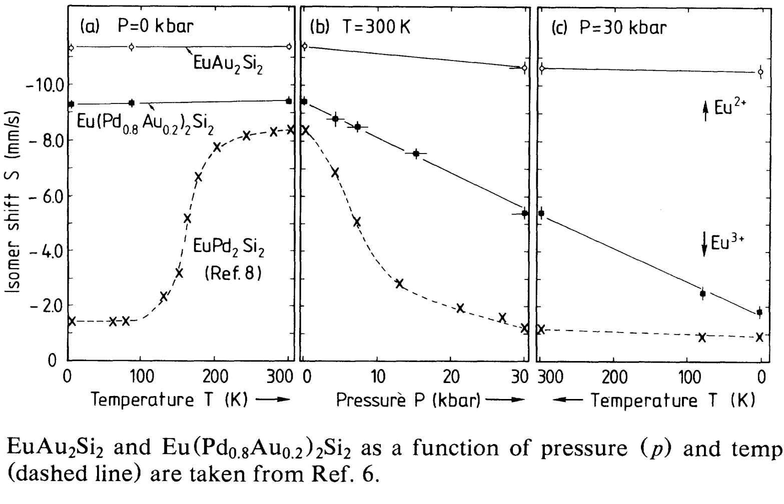

FIG. 2. Isomer shift of EuAu$_2$Si$_2$ and Eu(Pd$_{0.8}$Au$_{0.2}$)$_2$Si$_2$ as a function of pressure (p) and temperature (T). The corresponding data for EuPd$_2$Si$_2$ (dashed line) are taken from Ref. 6.

of the corresponding value found in typical IV compounds (e.g.,[7] EuCu$_2$Si$_2$, $\partial S/\partial p = +7\times10^{-2}$ mm/s·kbar). Figure 2(c) demonstrates the effect of temperature (300 to 4.2 K) on the valence state at a constant pressure of $p = 30$ kbar.

On the other hand, Eu(Pd$_{0.8}$Au$_{0.2}$)$_2$Si$_2$ reveals a further strong temperature shift (300 to 4.2 K) of the Eu valence towards the Eu^{3+} state. The large pressure- and temperature-induced changes of $\bar{S}$ in Eu(Pd$_{0.8}$Au$_{0.2}$)$_2$Si$_2$ demonstrate clearly the rapid *onset* of an IV behavior under application of high pressure. It has to be mentioned here that Eu(Pd$_{0.8}$Au$_{0.2}$)$_2$Si$_2$ is the first magnetically ordered Eu^{2+} compound which becomes IV at high pressure. All other known Eu compounds (e.g., EuCu$_2$Si$_2$,[7] EuRh$_2$,[8] and EuPd$_2$Si$_2$[6]) are nonmagnetic and display a temperature-dependent valence shift even at ambient pressure [see also Fig. 2(a)]. This anomalous temperature behavior of the valence at ambient pressure of our $x = 0.2$ sample is obviously related to the sign and magnitude of the energy separation (excitation energy) E_x between the Eu^{2+} and Eu^{3+} configurations. As mentioned before, from the χ measurements and the results for the ME isomer shift as a function of temperature at $p = 0$ kbar, it follows that the Eu ion in Eu(Pd$_{0.8}$Au$_{0.2}$)$_2$Si$_2$ is in a divalent $4f^7$ ground state, which should be located well below the $4f^6$ nonmagnetic (Eu^{3+}) state ($k_BT < E_x < 0$), so that no thermal admixture of the $4f^6$ state between 4.2 and 300 K can be observed.

To get a deeper insight into the valence behavior of the Eu(Pd$_{0.8}$Au$_{0.2}$)$_2$Si$_2$ system under high pressure, we want to analyze the pressure-induced change of the mean valence $\bar{v}(p)$ and the mean excitation energy $\bar{E}_x(p)$. In the framework of the interconfigurational fluctuation model,[9] the measured average isomer shift $\bar{S}$ of the IV state is given by[10]

$$\bar{S}(T,V) = S_2(T,V) + (S_3 - S_2)\bar{\nu}(T,V),$$

where S_2 and S_3 are the integral valence isomer shifts of the Eu^{2+} and Eu^{3+} states, respectively. The occupation probability of the $4f^6$ (Eu^{3+}) state $\bar{\nu}(T,V)$ (giving the mean valence $\bar{v} = 2 + \bar{\nu}$) can be derived from the measured $\bar{S}$ at 300 K and at different pressures, with suitable values for S_2 and S_3. We have chosen S_2 to be -11.4 mm/s, which is the isomer shift of the stable divalent EuAu$_2$Si$_2$ at 300 K in the same environment. For $S_2 - S_3$ a value of 13 mm/s is used.[11]

In order to obtain the real valence changes under pressure, $S_2(T,V)$ has been corrected for volume changes due to isothermal volume compression (-0.69 mm/s at 30 kbar) and chemical pressure caused by the Pd substitution ($+1.95$ mm/s for $\Delta V/V = 0.059$), with use of the measured $\partial S_2/\partial \ln V \simeq -31$ mm/s. Our calculations give values of $\bar{v}$ of 2.0, 2.2 ±0.1, and 2.4 ±0.1 for pressures of 0, 15, and 30 kbar at 300 K, respectively. These values can be used to evaluate $\bar{E}_x(p)$ at 300 K. The broadening of the ionic levels which is due to quantum mechanical hybridization and is described by the fluctuation temperature T_f is found to be small ($T_f \simeq 15$ K, from our χ measurements) compared to $\bar{E}_x$ at 0 kbar. Thus we used the relation[12]

$$\bar{\nu}(V,T) = \{1 + 8[1 + 3\exp(-480/T^*) + 5\exp(-1330/T^*)]^{-1}\exp[-\bar{E}_x(V,T)/k_BT^*]\}^{-1},$$

where $T^* = (T^2 + T_f^2)^{1/2}$; T_f is expected to depend on E_x (T_f should tend to zero[7] for $E_x \to \pm\infty$). Consequently, for an exact calculation of $\bar{E}_x(p)$ one should know $T_f(p)$ at 300 K, which would be obtained from measurements as a function of pressure, $\chi(p)$.[7] Despite the lack of data of $\chi(p)$ at 300 K for Eu(Pd$_{0.8}$Au$_{0.2}$)$_2$Si$_2$, a rough estimation of $\bar{E}_x(p)$ can be made by our assuming T_f to be constant with pressure, i.e., $\bar{E}_x(p)$ will include possible changes of $T_f(p)$. Performing such calculations, we obtain estimated values of $\bar{E}_x(p)$ of -600, 0, and $+330$ K for pressures of 0, 15, and 30 kbar, respectively. These results indicate a level crossing of the $4f^7$ (Eu^{2+}) state with the Fermi level E_F (the Eu^{3+} state is assumed to be located at E_F) around 15 kbar (or $\bar{v} \simeq 2.2$). The sign and magnitude of the calculated $\bar{E}_x(p)$ values are consistent with both the χ data and $\partial\bar{S}/\partial T$ at $p = 0$ kbar (see above).

The effect of pressure on the valence at 300 K can be understood now by the rapid change of $|\bar{E}_x|$ towards the $4f^6$ (Eu^{3+}) configuration. One can further explain the temperature-induced valence change at $p = 30$ kbar [Fig. 2(c)]. It follows from our calculation that $\bar{E}_x(p)$ becomes positive ($\sim +330$ K) at 30 kbar. A positive sign of $\bar{E}_x(p)$ implies that the $4f^7$ state is now located above the $4f^6$ state. In such a situation [as in EuPd$_2$Si$_2$; see Fig. 2(a)] the occupation probability of the $4f^6$ (Eu^{3+}) due to thermal admixture will increase on lowering of the temperature from 300 to 4.2 K. Consequently, the mean valence shifts towards the Eu^{3+} state [Fig. 2(c)], reaching a value of $\bar{v} \simeq 2.6$ at 4.2 K and at 30 kbar ($\bar{v}$ is found to be almost constant at $p = 54$ kbar).

Next, we turn to the most notable behavior of the system under high pressure, namely the breakdown of MO at 4.2 K. Figure 1(b) displays the ME spectra collected at 4.2 K and at different pressures. A dramatic collapse of the magnetic hf field at $p > 0$ kbar is clearly seen. This is the most important finding of the present work, namely the first observation of a pressure-induced breakdown of the magnetic Eu^{2+} state (due to a valence change) to the nonmagnetic IV state in a magnetically ordered Eu^{2+} compound. Figure 3 shows the pressure dependence of B_eff as obtained from the least-squares fits of the ME spectra.

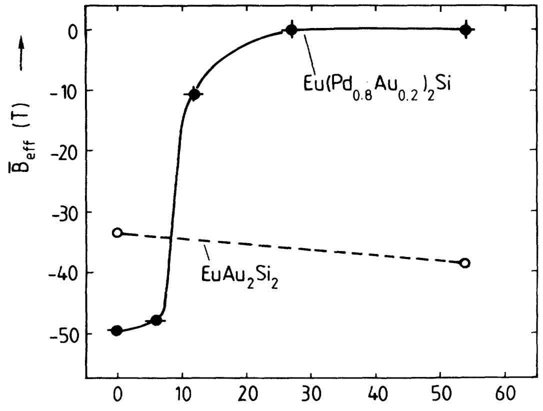

FIG. 3. Pressure dependence of $\bar{B}_{eff}$ at 4.2 K in Eu-(Pd$_{0.8}$Au$_{0.2}$)$_2$Si$_2$. Corresponding data for EuAu$_2$Si$_2$ extrapolated to $T = 0$ K are also shown.

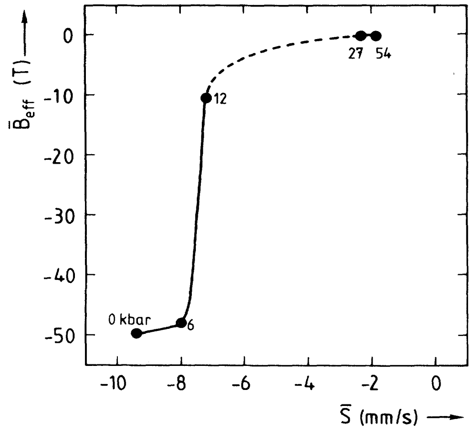

FIG. 4. Correlation between $\bar{S}$ and $\bar{B}_{eff}$ in Eu-(Pd$_{0.8}$Au$_{0.2}$)$_2$Si$_2$ at 4.2 K as a function of pressure.

The corresponding behavior of EuAu$_2$Si$_2$ is also shown for comparison. From Figs. 1(b) and 3, it is obvious that there is no MO for $p > 12$ kbar at 4.2 K. The range of coexistence of MO and IV in Eu-(Pd$_{0.8}$Au$_{0.2}$)$_2$Si$_2$ can be obtained by correlation of the values of $\bar{S}$ and $\bar{B}_{eff}$ at 4.2 K for different values of the pressure (Fig. 4). According to Fig. 4 the magnetic hf field vanishes at an isomer shift $\bar{S}$ of about -7 mm/s corresponding to an average valence of $\bar{v} \simeq 2.2$ at 4.2 K. This allows us to give the limits of the range of the mean valence $2 \leqslant \bar{v} \leqslant 2.2$ over which MO and IV can coexist in this magnetically ordered Eu^{2+} compound.

Finally, the last point which has to be discussed concerns the question of whether the observed collapse of MO is mainly caused by a pressure-induced suppression of the ordering temperature T_N or of the magnetic moment. From Fig. 4, it is evident that $\bar{v} \simeq 2.2$ is the maximum allowed mean valence which can coexist with MO. Assuming that the system fluctuates between the $J = 0$ (Eu^{3+}) and $J = \frac{7}{2}$ (Eu^{2+}) states, a value of $\bar{v} \simeq 2.2$ would correspond to a reduction of the average magnetic moment ($7\mu_B$) by about 20%. On the other hand, the pressure suppression of T_N is found to be extremely large: $T_N = 32$ K at $p = 0$ kbar and $T_N << 4.2$ K at $p > 12$ kbar. This demonstrates clearly that the collapse of MO is caused by the pressure-induced suppression of T_N rather than of μ. It is interesting to note that this last finding is in qualitative agreement with a recent theoretical calculation (*sf* exchange and hybridization model) by Matlak and Nolting.[13] According to this model the breakdown of the MO in the IV phase should be due to electronic fluctuations rather than to the reduction of the magnetic moment. We feel that the above results may stimulate further theoretical efforts concerning the problem of the coexistence between IV and MO.

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[a] Present address: Institut für Experimentalphysik IV, Universität Bochum, D-4630 Bochum 1, West Germany.

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