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Anomaly of the quadrupole interaction in mixed-valence $EuPd_2Si_2$

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The homogeneous mixed-valence compound $EuPd_2Si_2$ has been studied thoroughly at temperatures $4.2\ \mathrm{K} \leq T \leq 292\ \mathrm{K}$ with use of the ^{151}Eu Mössbauer effect. In the temperature region of the valence transition at $T \approx 160$ K a maximum of the quadrupole interaction and of the linewidth has been observed. This effect is attributed to an enhanced admixture of $4f$ contributions to the conduction-electron states, which therefore exhibit stronger non-s character. At $T = 160$ K and in an external magnetic field of 12.8 T, a small field-induced valence shift towards Eu^{2+} has been observed, as indicated by a change of the isomer shift of $\Delta S = 0.20(4)$ mm/s.

I. INTRODUCTION

By Mössbuaer effect[1] and L_{III} x-ray absorption[2] measurements it has been well established that $EuPd_2Si_2$ can be characterized as a homogeneous mixed-valence system with a thermally driven valence change near 150 K. This intermetallic compound crystallizing in the tetragonal $ThCr_2Si_2$ structure is of special interest among the Eu-based mixed-valence compounds due to the narrow temperature range in which the valence changes considerably from about 2.9 at 80 K to about 2.2 at 300 K.[1] The valence change with temperature is also revealed by the lattice parameters and the magnetic susceptibility[3] and by photoemission spectroscopy.[4] Furthermore, the valence transition can be induced by applying high pressure. In this way from Mössbauer-effect[5] and electrical-resistivity[6,7] measurements under pressure a pressure-temperature phase diagram has been derived proposing a first-order phase transition at "negative" pressures, i.e., for an expanded lattice. By comparison with the valence shift of the diluted compound $Eu_{0.01}La_{0.99}Pd_2Si_2$ Croft *et al.*[8] suggested a cooperative coupling between the Eu ions in the concentrated compound $EuPd_2Si_2$.

Most of these experiments have been explained in terms of the ionic interconfigurational fluctuation (ICF) model.[9–11] In this model it is assumed that the valence of the Eu ions fluctuates between the integral values $v = 2$ and $v = 3$ on a time scale of $10^{-13}-10^{-15}$ s. The Mössbauer effect with a typical measuring time of about 10^{-8} s displays therefore a motionally narrowed single absorption line with a mean isomer shift corresponding to a time average of the two integral values of the valence. On this basis one would expect that also the quadrupole interaction observed in the Mössbauer spectra should reveal the time average of the values of Eu^{2+} and Eu^{3+}. Such a "mean" quadrupole interaction should change smoothly with temperature according to the behavior of the isomer shift and valence, respectively. However, our ^{151}Eu Mössbauer-effect experiments on $EuPd_2Si_2$ as a function of temperature yielded a distinct maximum of the quadrupole interaction in the temperature range where the valence shift takes place. In the present work we would like to show that this effect cannot be fully described by the ICF model.

II. EXPERIMENTAL

We have performed ^{151}Eu Mössbauer-effect experiments in the temperature range $4.2 \leq T \leq 292$ K, using a polycrystalline $EuPd_2Si_2$ absorber (20.9 mg/cm^2 of $EuPd_2Si_2$) and a 700-mCi $^{151}Sm_2O_3$ soruce. The temperature has been stabilized better than 0.1 K at low temperatures and 0.3 K at high temperatures. The x-ray diffraction analysis of the absorber material showed the correct tetragonal $ThCr_2Si_2$ structure with lattice parameters at room temperature of $a = 0.4231(5)$ nm and $c = 0.9860(5)$ nm in good agreement with Ref. 3. A chemical analysis by means of plasma-emission spectroscopy, yielded for the stoichiometry of the sample 17.26(28) at.% Eu, 40.50(36) at.% Pd, and 42.15(53) at.% Si (ideally 20:40:40 at.%, respectively). Thus the sample showed a small excess of Si and a corresponding deficiency of Eu. To study the influence of high-magnetic fields, several Mössbauer-effect spectra have been taken at different temperatures by applying an external field of 12.8 T on the absorber.

III. RESULTS

Typical ^{151}Eu Mössbauer-absorption spectra of our $EuPd_2Si_2$ sample measured at different temperatures in zero external field are shown in Fig. 1. All spectra are composed by an asymmetric main component and by a weak ($\simeq$14% of the total area) satellite line. These spectra have been fitted by quadrupole-split ^{151}Eu spectra for both the main component and the satellite line. According to the theoretical form of the quadrupole splitting of ^{151}Eu, each of these two subspectra has been composed by a superposition of eight Lorentzian lines. For these Lorentzian lines we have assumed the theoretical line intensities and equal linewidth (modified by absorber-thickness effects). To avoid confusion later, we will denote the width of these Lorentzian lines by Γ_0. The satellite line broadens considerably at low temperatures, indicating magnetic ordering.[12] Therefore a magnetic hy-

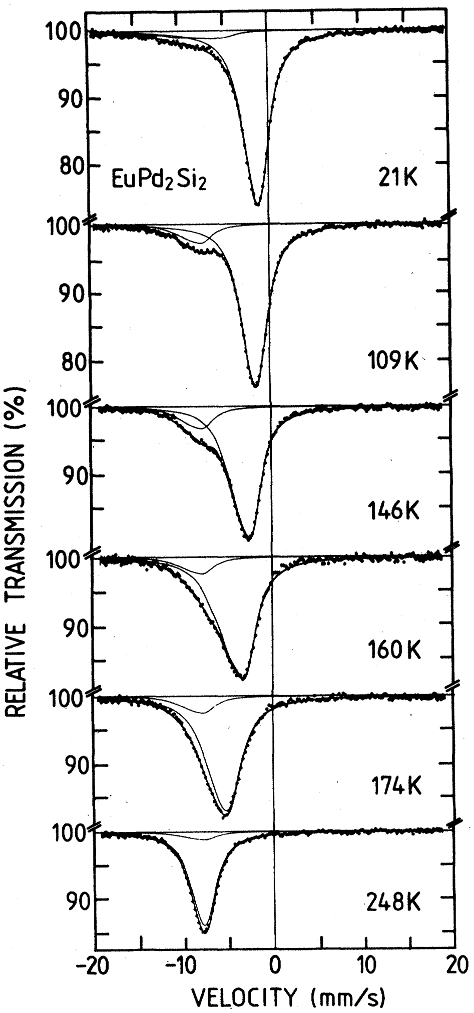

FIG. 1. ^{151}Eu Mössbauer spectra of $EuPd_2Si_2$ at different temperatures in zero external magnetic field. The solid lines represent the two fitted subspectra and the superposition of the subspectra, respectively. At high temperatures where the satellite line strongly overlaps with the main line, the position and intensity of the satellite has been kept fixed in the fitting procedure.

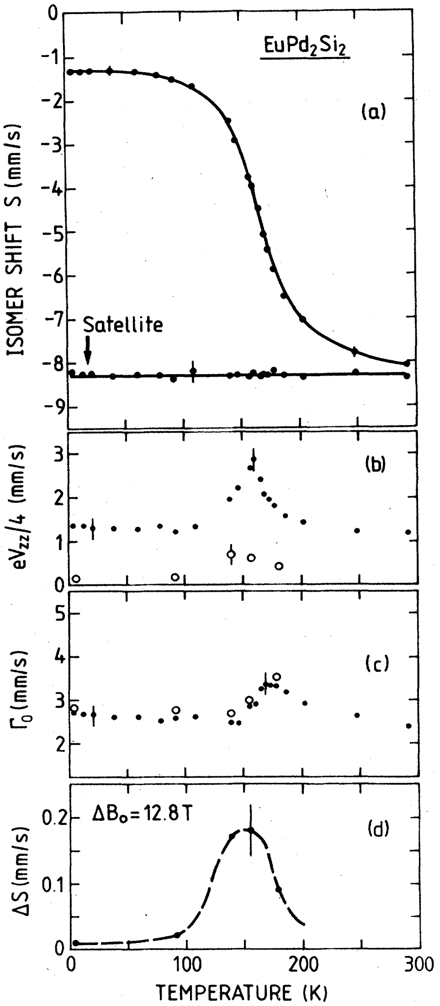

FIG. 2. Temperature dependence of several properties of the main resonance line: (a) isomer shift S (the isomer shift of the satellite line is shown also); (b) electric field gradient $eV_{zz}/4$ in zero external magnetic field $B_0=0$ T (●) and $B_0=12.8$ T (○); (c) Mössbauer linewidth Γ_0 (see text) in zero field $B_0=0$ T (●) and $B_0=12.8$ T (○); (d) Change ΔS of the isomer shift in an external magnetic field $B_0=12.8$ T with respect to the zero-field data. All curves drawn are guides for the eye only.

perfine splitting of the satellite has been included into the fitting procedure for spectra at $T<80$ K. The main component, on the other hand, did not show considerable line broadening for $T<80$ K and therefore is expected to remain nonmagnetic.

Figure 2(a) shows the isomer shift S as a function of temperature. The isomer shift of the main component changes from $S=-1.38$ mm/s at 4.2 K to $S=-8.10$ mm/s at 292 K, demonstrating the valence instability of $EuPd_2Si_2$. Regarding the different ^{151}Sm sources used, these data agree fairly well with the data of Refs. 1 and 5. The small deviation of the room-temperature value may be due to different treating of the satellite line within the fitting procedure. This satellite strongly overlaps with the main component at high temperatures.

So far in all Mössbauer investigations of $EuPd_2Si_2$ (Refs. 1 and 5), a distinct satellite line beside the main resonance line has been observed. In the x-ray analysis of our sample we could not detect any traces of another Eu phase with different crystal structure. Because the sample showed only about 2-at. % deviation from the ideal stoichiometry, we believe that the satellite line should be due to another Eu configuration, which may be caused by disordering or site exchange of the Pd and Si ions. A similar explanation has been given for the satellite line observed in $EuCu_2Si_2$.[13] Our isomer shift data of this satellite are plotted in Fig. 2(a) also. The value of $S=-8.3$ mm/s remains nearly constant throughout the whole temperature range.

In contrast to Schmiester *et al.*,[5] we could not observe any valence shift of the satellite. On the other hand, we have found an increasing line broadening of the satellite below $T \simeq 80$ K which can be explained by magnetic ordering of the satellite phase. Thus we feel that the observed[5] shift of the position and the decrease of the intensity of the satellite line may be not real, but could have been masqueraded by the magnetic hyperfine splitting.[12]

From Fig. 1 it is obvious that the total width of the main resonance line broadens asymmetrically in the temperature range around $T=160$ K. This broadening can be attributed mainly to the temperature dependence of the quadrupole interaction which reveals a maximum at $T=160$ K (120% increase with respect to the base line), as shown in Fig. 2(b). The reasons for this attribution are discussed in more detail in Sec. IV. One formal but nevertheless relevant reason is that for all spectra the feature of asymmetric broadening can be fitted sufficiently well only by assuming an enhanced quadrupole interaction. The χ^2 values of such a fitting procedure amount to 0.85 to 0.95 for all spectra. In contrast, fitting the spectra, e.g., by keeping the quadrupole interaction independent of temperature, and allowing (i) the increase of the linewidth Γ_0 of the main component or (ii) the increase of the intensity (which is physically not reasonable) and varying the position and linewidth Γ_0 of the satellite component always yields definitely worse χ^2 values of 1.5 to 1.7.

By applying an external magnetic field of $B_0=12.8$ T, the maximum of the quadrupole interaction is suppressed [Fig. 2(b)]. In addition, the linewidth Γ_0 shows also a maximum in this temperature range [Fig. 2(c)]. Here, Γ_0 again denotes the width of the eight Lorentzian lines composing the quadrupole-split ^{151}Eu spectrum which has been fitted to the main resonance line. All fitting results of our spectra are compiled in Table I.

In a high external magnetic field the isomer shift S as a function of temperature exhibits small deviations from the corresponding zero-field values in the temperature range where the valence transition occurs. These deviations show a maximum of $\Delta S=0.20(4)$ mm/s at $T \simeq 155$ K [Fig. 2(d)], indicating a valence shift of $\Delta v=0.017(3)$ toward Eu^{2+} in an external field of $B_0=12.8$ T. A similar effect has been found in the mixed-valence compound EuCu$_2$Si$_2$ also in the temperature range of the valence transition.[14] This has been explained by the reduction of the interconfigurational excitation energy E_x due to the Zeeman splitting of the Eu^{2+} $4f^7$ level in a magnetic field.[14]

IV. DISCUSSION

We would like to attribute the distinct line broadening of the Mössbauer spectra (Fig. 1) near $T=160$ K predominately to an increase of the quadrupole interaction in this temperature range [Fig. 2(b)]. This interpretation is supported by three facts.

(i) The spectra cannot be fitted sufficiently well, based on other assumptions (see above).

(ii) Relaxation processes cannot explain the asymmetric broadening because the valence fluctuations of the system take place on a time scale of $10^{-13}-10^{-15}$ s. Therefore, the comparatively slow Mössbauer effect ($\sim 10^{-8}$ s) will display motionally narrowed lines averaging on the valence-fluctuation phenomena.

TABLE I. Isomer shift S, quadrupole interaction $eV_{zz}/4$, and linewidth Γ_0 of the main component of EuPd$_2$Si$_2$ as a function of the temperature in externally applied magnetic fields $B_0=0$ T and $B_0=12.8$ T. The isomer shift is given with respect to a ^{151}Sm$_2$O$_3$ source. The errors given indicate the standard deviations obtained by the least-squares fit.

	S (mm/s)		$eV_{zz}/4$ (mm/s)		Γ_0 (mm/s)	
T (K)	$B_0=0$ T	$B_0=12.8$ T	$B_0=0$ T	$B_0=12.8$ T	$B_0=0$ T	$B_0=12.8$ T
4.2	−1.35(1)	−1.36(3)	1.37(5)	0.16(9)	2.73(4)	2.84(5)
12.6	−1.35(2)		1.37(8)		2.68(6)	
21.0	−1.33(1)		1.30(6)		2.66(4)	
39.0	−1.32(1)		1.30(5)		2.61(3)	
60.0	−1.36(1)		1.28(6)		2.62(4)	
79.0	−1.44(1)		1.35(6)		2.54(4)	
92.5	−1.53(1)	−1.55(3)	1.23(9)	0.10(10)	2.56(7)	2.73(4)
109.0	−1.67(1)		1.35(5)		2.62(4)	
140.0	−2.50(1)	−2.67(4)	1.95(4)	0.65(10)	2.48(4)	2.68(6)
146.0	−2.95(1)		2.22(5)		2.48(4)	
157.0	−3.78(2)	−3.96(6)	2.70(5)	0.59(16)	2.86(4)	3.01(8)
160.0	−3.99(5)		2.89(12)		2.85(7)	
166.0	−4.50(2)		2.42(8)		3.25(7)	
169.5	−5.08(3)		2.06(12)		3.38(10)	
173.5	−5.46(2)		1.99(10)		3.34(9)	
178.0	−5.90(2)	−5.99(6)	1.82(8)	0.46(25)	3.33(6)	3.50(10)
187.5	−6.52(2)		1.56(13)		3.19(10)	
203.0	−7.06(2)		1.45(9)		2.92(7)	
248.0	−7.80(2)		1.23(8)		2.64(6)	
292.0	−8.06(2)		1.23(8)		2.41(6)	

(iii) In an external magnetic field the asymmetric line broadening is suppressed as shown in Fig. 2(b). This can be explained easily, because in a polycrystalline sample the quadrupole interaction being fixed with respect to the randomly oriented main symmetry axis of the crystal, is averaged to a zero mean value in the presence of an external magnetic field defining the axis of quantization. Therefore, one will observe in this case instead of a homogeneous quadrupole shift an inhomogeneous broadening of the linewidth Γ_0. In fact, as shown in Fig. 2(c) a slight increase of Γ_0 has been observed for the spectra measured in an external field of 12.8 T.

In order to analyze in detail the temperature dependence of the quadrupole interactions, we will discuss first the different contributions to the electric field gradient (EFG) and then the influence of the temperature on each.

For an axial symmetric crystal such as $EuPd_2Si_2$, the quadrupole interaction is given by

$$E_Q=\frac{eV_{zz}}{4}\frac{Q}{I(2I-1)}[3I_z^2-I(I+1)]\ , \qquad (1)$$

where $V_{zz}=d^2V/dz^2$ is the EFG, e is the electron charge, Q is the nuclear quadrupole moment, and I is the nuclear spin quantum number. For an intermetallic $4f$ compound the EFG is composed of three contributions:[15]

$$V_{zz}=(1-R)q_{4f}+(1-\gamma)q_{\text{latt}}+(1-R')q_{\text{CE}}\ . \qquad (2)$$

Here, R, R', and γ are Sternheimer shielding factors and q_{4f}, q_{latt}, and q_{CE} denote the contributions to V_{zz} of the $4f$ shell, of the ionic charges of the lattice, and of the conduction electrons, respectively. We would like to discuss now, which of these contributions may be responsible for the observed maximum of $E_Q(T)$.

Let us start with the second term, namely, the EFG contribution q_{latt} of the crystal. Due to the tetragonal crystal structure, one expects $q_{\text{latt}}\neq 0$. From lattice-parameter measurements[3] it is known that with decreasing temperature (300 to 80 K) the lattice parameter c increases slightly by 0.1% whereas the parameter a decreases considerably by 1.6%, reflecting the valence transition. Hence, the c/a ratio increases by 1.7%. For a hexagonal close-packed lattice of ions with charge Ze one can calculate[16] q_{latt} from

$$q_{\text{latt}}=Ze[0.0065-4.3584(c/a-1.633)]/a^3\ . \qquad (3)$$

Adapting this relation to the tetragonal lattice of $EuPd_2Si_2$, we can estimate that q_{latt} should increase by about 10% from 300 to 80 K due to the change of the c/a ratio. This effect may cause the small slope of the base line of $eV_{zz}/4$ plotted in Fig. 2(b). One may speculate that the valence transition could be accompanied by small lattice distortions which should lead to an enhancement of q_{latt}. But our estimation shows that such a mechanism can give a contribution of the order of 10–20% only. Hence, we conclude that the lattice contribution to the EFG cannot account for the observed maximum which is a 120% effect with respect to the base line [Fig. 2(b)].

Next, we would like to discuss the contribution q_{CE} of the conduction electrons to the EFG. $EuPd_2Si_2$ is metallic on both sides of the valence transition, i.e., in the approximately divalent and trivalent state. Consequently, the contribution q_{CE} of the conduction electrons belonging to the integer valence states must be already included in the measured EFG values of the base line in Fig. 2(b). Furthermore, Sampathkumaran *et al.*[17] concluded from ^{63}Cu-NMR measurements on $EuCu_2Si_2$ as a function of temperature, that in this compound the conduction electrons can be considered as nearly free electrons. In the limit of free electrons the conduction-electron distribution is isotropic and cannot display any quadrupole potential. Therefore, based on these arguments we expect by cursory examination no relevant contribution q_{CE} of the conduction electrons.

We are left with the contribution q_{4f} of the Eu ion's own $4f$ shell. The $^8S_{7/2}$ ground state of pure Eu^{2+} cannot create any EFG at the Eu nucleus. The same holds for the $J=0$ ground state of the Eu^{3+} $4f^6$ configuration. However, according to Elliott[18] the $J=2$ excited multiplet state of Eu^{3+} will be mixed into the $J=0$ ground state by the action of a crystalline field and can produce in this way an EFG in second-order perturbation theory. This EFG contribution in Eu^{3+} is proportional[18] to $1/\Delta_2$, where Δ_2 ($=1330$ K for Eu^{3+}) denotes the energy separation between the $J=0$ and $J=2$ levels. From this situation one would expect that $(1-R)eq_{4f}/4$ nearly vanishes at room temperature for $EuPd_2Si_2$ (divalent side) and shows a certain small value at 4.2 K which must be less than the base line value of 1.35 mm/s according to Fig. 2(b). By a cursory examination, within the frame of the ICF model (Refs. 9–11) the EFG is expected to display in the intermediate temperature range a time average (due to the comparatively slow Mössbauer-effect time scale) of these two limiting values. This average EFG should simply reflect the temperature dependence of the valence. Therefore, no maximum of the EFG would be expected.

None of the mechanisms discussed so far can explain even qualitatively the observed maximum of the EFG. However, applying the ICF model more carefully one can find arguments for this effect. In this model the ionic level schemes of the $4f^6$ and $4f^7$ configurations are assumed to coexist. Both configurations are separated by the interconfigurational excitation energy E_x. The system is assumed to fluctuate between both configurations on a time scale of 10^{-13} to 10^{-15} s, causing a broadening of the ionic levels (due to the finite lifetime) by a "mixing width" $\Gamma_m=k_BT_f$ (T_f equals the "fluctuation temperature"). Both T_f and E_x are functions of the temperature. Now, the broadening of the $4f^6$ ionic levels expressed by T_f will reduce the effective energy separation Δ_2 between the $J=0$ and $J=2$ states of Eu^{3+} and will therefore increase the EFG. As worked out from isomer shift and magnetic susceptibility data,[5] T_f as a function of temperature exhibits a maximum at about $T=100$ K with a value of T_f(max) 200 K. Such a maximum of $T_f(T)$ causes a minimum of $\Delta_2(T)$ and could therefore explain qualitatively the observed temperature dependence of the EFG. Assuming an equal value of $T_f=200$ K for the $J=0$ and $J=2$ levels the energy gap Δ_2 would be reduced by about $2T_f/2=200$ K from 1330 K (Eu^{3+}) to about $\Delta_2=1100$ K in the region of the valence transition. Due to the relation $q_{4f}\sim 1/\Delta_2$ valid for Eu^{3+} (Ref. 18) the EFG should increase by a factor $1330/1100=1.2$. Based on the measured low-temperature value of $eV_{zz}/4=1.35$ mm/s which can be regarded as an upper limit for the EFG of Eu^{3+} we estimate then a maximum value of 1.62 mm/s for the EFG at the valence transition temperature. This has to be compared with our experimental value of 2.9 mm/s [Fig. 2(b)]. In judging the reliability of this estimate, one should keep in mind that the evaluation of T_f as performed in Ref. 5 depends sensitively on the presence of the satellite phase and on its magnetic properties.[12,14] On the other hand, to explain quantitatively the observed EFG maximum by this model, one would need a value of $T_f \simeq =1200$ K for the width of the $J=2$ level. However, such a value of T_f being comparable with the ionic level distance of the $J=2$ state (1330 K) would be unreasonably large.

As yet we have argued in terms of ionic level schemes only and have neglected the properties of the conduction electrons, assuming that the valence transition from the $4f^7$ to the $4f^6+e$ configuration involves nearly free electrons only. However, according to the Anderson approach to a virtual bound state, often the consideration is made[11] that with decreasing temperature at the valence transition the $4f^7$ state of Eu sweeps through the Fermi level. In this instant the $4f^7$ state will strongly hybridize with the conduction-band states. Hence, the hybridized wave function certainly will contain more contributions of non-s character (d,f contributions). Such not completely delocalized "conduction" electrons with non s character obviously can produce an EFG at the Eu nucleus. This effect will be largest in the region of the valence transition. The same conclusion follows from a somewhat different point of view. At the valence transition the sample contains trivalent and divalent Eu Ions. Regarding the Eu^{3+} ions as impurities with an effective electronic charge $+1$, these charges must be screened by a conduction-electron cloud.[19] It has been suggested by de Châtel,[20] that this screening charge may also contain components of electrons with orbital moments up to $l=3$ to a certain degree. In other words, the separation of the EFG into three distinct contributions carried out in Eq. (2) may not be adequate in the valence transition region. Instead, a further term should be added taking into account the mixing of localized $4f$ states and delocalized conduction-band states.

From these arguments one can understand why the ICF model cannot explain the observed temperature dependence of the EFG sufficiently. The quadrupole interaction as measured by the Mössbauer effect reacts sensitively on both the changes of the $4f$ shell and on the related character of the conduction electrons. The ICF model, however, considers only the density of states at the Fermi level as a parameter determining the strength of the valence mixing. But it does not really take into account the nature of the conduction electrons.

Finally, we would like to discuss the broadening of the resonance line shown in Fig. 2(c). The linewidth Γ_0 exhibits a maximum at about 170 K which seems to be slightly shifted with respect to the maximum of the quadrupole interaction. However, this shift may be artificial within the limits of error and may have no meaning. In contrast to the maximum of the qaudrupole interaction, which is a homogeneous effect, the observed peak of the linewidth must be an inhomogeneous effect. We believe that it can be caused by local inhomogeneities of the EFG and/or of the isomer shift during the valence transition. Due to crystal imperfections, impurities, dislocations, etc., the valence transition will take place in the crystal at different sites at slightly different temperatures reducing the sharpness of the valence transition.

From the arguments given above it follows consequently that such maxima of the EFG and the linewidth should appear, independently of whether the valence transition has been induced by changing the temperature or by applying pressure. Indeed, looking carefully on the Mössbauer spectra of $EuPd_2Si_2$ published by Schmiester *et al.*,[5] a line broadening can clearly be seen at the pressure where the valence changes are strongest. This effect has not been discussed by the authors.

V. CONCLUSION

Our Mössbauer measurements have shown that the valence transition of $EuPd_2Si_2$ is accompanied by a maximum of the quadrupole interaction and of the resonance linewidth. To explain this effect, we propose that at the valence transition a hybridization between the $4f^7$ state and the conduction-band states takes place. As result of this hybridization the conduction-band states will contain admixtures of non-s character with orbital moments up to $l=3$. Such components with $l \neq 0$ can produce an electric field gradient at the Eu nucleus. The ICF model which has been used to explain most of the experimental data regarding the mixed valence behavior of such compounds, so far, does not take into account the detailed character of the conduction electrons. That might be the reason why it cannot describe the observed EFG anomaly satisfactory. The present work demonstrates that the quadrupole interaction as measured by the Mössbauer effect can provide valuable information about the valence-fluctuation phenomena in mixed-valence Eu compounds.

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