

Interplay between structural, electronic, and magnetic instabilities in EuT_2P_2 ($T = \text{Fe, Co}$) under high pressure

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^{151}Eu (and ^{57}Fe) high-pressure Mössbauer investigations on EuFe_2P_2 reveal that the pressure-induced isostructural phase transition $3 \lesssim p \lesssim 9$ GPa is accompanied by a continuous valence transition from Eu^{2+} to Eu^{3+} with the consequence of the disappearance of the $\text{Eu}(4f)$ sublattice moment. However, contrary to EuCo_2P_2 we find in the high-pressure phase of EuFe_2P_2 no magnetic moment on Fe. Volume-dependent band-structure calculations in both systems show that the formation of the $3d$ moment strongly depends on the position of the $3d$ states relative to the Fermi energy and that the filling of the $3d$ states in EuCo_2P_2 is mainly caused by the $P-3p$ electrons.

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The rare-earth (RE) transition metal (T) phosphides, $RET_2\text{P}_2$, crystallizing in the ThCr_2Si_2 -type structure belong to an interesting class of materials in which structural instability is intimately connected with electronic and magnetic instabilities. These strong electron correlations lead to the formation of a large variety of ground states in this series. Depending on the type of RE and/or T , one observes not only different magnetic phenomena such as $4f$ -sublattice magnetism (EuCo_2P_2),¹ $3d$ -sublattice magnetism (LaCo_2P_2)² or magnetism of both sublattices (PrCo_2P_2),³ but also intermediate valent behavior (EuNi_2P_2)⁴ or even superconductivity (LaRu_2P_2).⁵ Essentially responsible for such a broad variety of properties is the ability of the ThCr_2Si_2 structure to adapt to several elements with various atomic sizes resulting in extremely different lattice parameters. In fact, within the $RET_2\text{P}_2$ series, there exists two extremely dissimilar P-P distances along the c axis resulting in two isostructural phases: α phase for a large P-P distance ($d_{\text{P-P}} \approx 2.8$ Å) with a non-bonding P-P state; and β phase for a short $d_{\text{P-P}} \approx 2.3$ Å forming a P-P single bond state.⁶ Structural phase transitions of first- and second-order between these phases can easily be induced by changing composition,⁷ temperature,⁸ or applying external pressure.⁹ According to recent band-structure calculations on some $RET_2\text{P}_2$ compounds such structural phase transitions strongly affect the electronic structure of these systems.¹⁰

Towards understanding such an interplay in $RET_2\text{P}_2$ systems, we have recently performed high-pressure experiments (^{151}Eu Mössbauer spectroscopy and x-ray diffraction) on the magnetically ordered compound EuCo_2P_2 .¹¹ In this system, antiferromagnetism is due to ordering of the Eu^{2+} ($^8\text{S}_{7/2}$) sublattice moments ($T_N = 66.5$ K) while the $\text{Co}(3d)$ sublattice exhibits no magnetic moments. Here, high-pressure experiments demonstrated that the pressure-induced first-order

structural ($\alpha \rightarrow \beta$) phase transition at $p > 3$ GPa is connected with a sharp valence transition of Eu from magnetic Eu^{2+} to a nonmagnetic Eu^{3+} ($^7\text{F}_0$) state. As a consequence, the disappearance of the $\text{Eu}(4f)$ sublattice magnetism is accompanied by a simultaneous appearance of $\text{Co}(3d)$ sublattice magnetism with $T_N^* = 260$ K.¹¹

These experimental findings, however, raise crucial questions that have to be addressed in order to shed light into the nature of electron correlations in these class of materials: (a) Is a first-order structural phase transition necessary for the occurrence of the pressure-induced change of sublattice magnetization ($4f \rightarrow 3d$), (b) does the formation of the $3d$ moment under high pressure depend on the type of transition metal (Fe, Co, Ni), and (c) what causes the filling of the $3d$ states?

In order to provide an answer to these questions, we have performed ^{151}Eu (and ^{57}Fe) high-pressure Mössbauer effect (ME) experiments on the ferromagnetic compound EuFe_2P_2 ($T_C = 27$ K).² The ME technique allows to investigate simultaneously possible pressure-induced variations of the valence state of Eu ($\text{Eu}^{2+} \rightarrow \text{Eu}^{3+}$) via the ME isomer shifts S and of the magnetism of the Eu and Fe sublattices, via the effective magnetic hyperfine field, B_{eff} , at the ^{151}Eu and ^{57}Fe nuclei, respectively. EuFe_2P_2 is an excellent candidate for such investigations. At ambient pressure the magnetic and electronic properties of EuFe_2P_2 are common with those of EuCo_2P_2 : magnetic order of EuFe_2P_2 is also due to ordering of the Eu^{2+} sublattice moment while Fe does not carry any magnetic moment.² However, in contrast to EuCo_2P_2 the pressure-induced structural ($\alpha \rightarrow \beta$) phase transition in EuFe_2P_2 is continuous for $3 \text{ GPa} \lesssim p \lesssim 9 \text{ GPa}$.¹² Thus, the investigation of the influence of the pressure-induced structural phase transition on the electronic and magnetic properties of EuFe_2P_2 in comparison with EuCo_2P_2 should provide

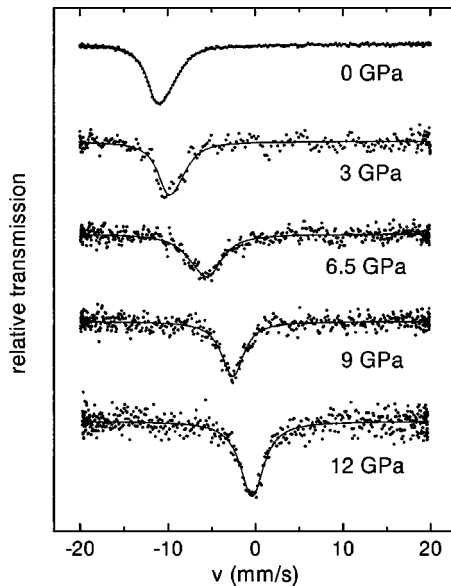


FIG. 1. ^{151}Eu Mössbauer spectra of EuFe_2P_2 collected at 300 K and at different pressures.

valuable information on the nature of strong electron correlations in these compounds. To obtain a theoretical interpretation of the experimental results, we have performed volume-dependent band-structure calculations on EuFe_2P_2 and EuCo_2P_2 .

A polycrystalline single phase EuFe_2P_2 sample was prepared as described elsewhere.¹³ ^{151}Eu (^{57}Fe) high-pressure ME measurements were performed up to 12 GPa at 300 and 4.2 K using a diamond anvil cell (DAC).¹⁴ ME sources ($^{151}\text{SmF}_3 \cong 100$ mCi and ^{57}Co in $\text{Rh} \cong 10$ mCi) and absorbers were kept during the measurements at the same temperature. Figure 1 shows some selected ^{151}Eu ME spectra collected at 300 K in the pressure range $0 \leq p \leq 12$ GPa in which the pressure-induced structural ($\alpha \rightarrow \beta$) phase transition takes place.¹² The ME parameters at ambient pressure and 300 K are in a very good agreement with those previously published.² As evident from Fig. 1, there is large pressure-induced change of the isomer shift from $S = -10.7$ (2) mm/s at 0 GPa to -0.4 (1) mm/s at 12 GPa. This clearly indicates a change of the valence state of Eu with increasing p from the Eu^{2+} state towards Eu^{3+} . The analysis of the pressure-induced change of S is displayed in Fig. 2. As shown in the figure, the rate of change of S with increasing pressure is enhanced above $p \approx 3$ GPa indicating the onset of valence transition. This is consistent with the change of the lattice parameter a with pressure (see inset of Fig. 2), which shows that the anisotropic increase of the lattice parameter a sets in at about $p \approx 3$ GPa and ends before decreasing at $p \approx 9$ GPa.¹² The lattice parameter c decreases drastically ($\Delta c/c \approx 13\%$) as a consequence of the $\alpha \rightarrow \beta$ phase transition. From this we can conclude that the second-order structural phase transition in EuFe_2P_2 is connected with a continuous valence change of Eu from Eu^{2+} to Eu^{3+} .

As mentioned above, in the case of EuCo_2P_2 the pressure-induced valence transition $\text{Eu}^{2+} \rightarrow \text{Eu}^{3+}$ was found to be accompanied by a simultaneous appearance of $\text{Co}(3d)$ magne-

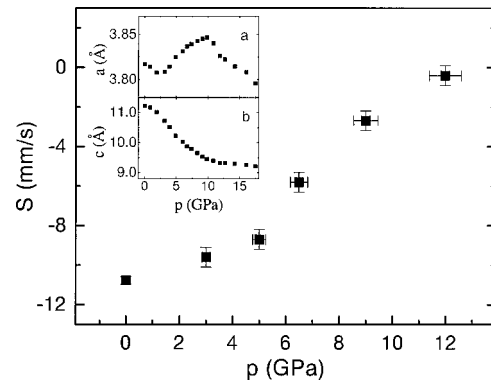


FIG. 2. Pressure dependence of the ^{151}Eu Mössbauer isomer shift S at 300 K as deduced from the least square fits of the measured ME spectra. The inset shows the anisotropic variation of lattice parameters a and c of EuFe_2P_2 with pressure according to Ref. 12.

tism. In order to inspect whether the same magnetic phenomena occurs in EuFe_2P_2 [i.e., appearance of $\text{Fe}(3d)$ magnetism], we have performed ^{151}Eu and ^{57}Fe high-pressure ME experiments at 4.2 K and at 9 GPa. Figure 3(a) displays ^{151}Eu ME spectra collected at 0 and 9 GPa and at 4.2 K. At ambient pressure we find, as expected, a magnetically split Eu^{2+} spectrum which is due to the ordering of the Eu^{2+} moments below T_C . Both values of B_{eff} (-30.3 T) and S (-10.6 mm/s) are in a very good agreement with those already published.² At 9 GPa and 4.2 K (the high-pressure β phase) the magnetic hf splitting disappears, one observes a single quadrupole broadened absorption line located at $S \approx -0.9$ mm/s corresponding to the Eu^{3+} state. These results

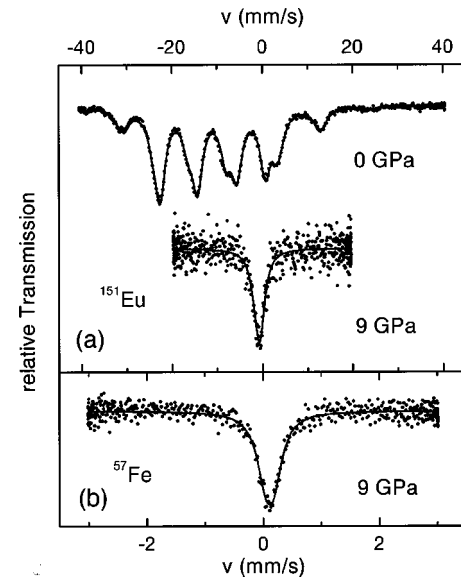


FIG. 3. (a) ^{151}Eu Mössbauer spectra ($T=4.2$ K) at ambient pressure and 9 GPa. The magnetic hf splitting at $p=0$ GPa corresponds to the Eu^{2+} , whereas the single line absorption (nonmagnetic) corresponds to the Eu^{3+} state. (b) ^{57}Fe Mössbauer single line absorption spectrum in the high-pressure phase (β phase) of EuFe_2P_2 at 9 GPa and 4.2 K, which shows that the Fe sublattice does not exhibit magnetic moments.

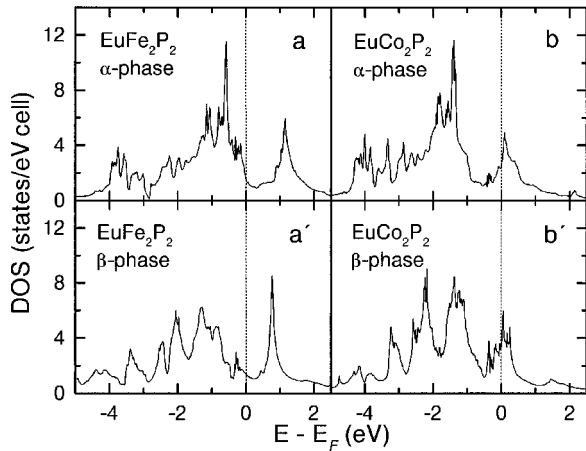


FIG. 4. Calculated total $3d$ density of states (DOS) of Fe in EuFe_2P_2 (a, a') and Co in EuCo_2P_2 (b, b') both at ambient pressure (α phase) and in the high-pressure phase (β phase), respectively. Dashed lines at $E - E_F = 0$ mark the position of the Fermi energy E_F .

clearly demonstrate the disappearance of the $\text{Eu}(4f)$ sublattice magnetism in the high-pressure phase of EuFe_2P_2 . In order to search for a possible existence of Fe sublattice magnetic moment in the high-pressure phase of EuFe_2P_2 , we have performed ^{57}Fe ME measurement at 9 GPa (4.2 K) on the same sample in the DAC. As evident from Fig. 3(b) one also observes a single line absorption pattern, indicating that the Fe sublattice does not exhibit any magnetic moment in the high pressure (β) phase of EuFe_2P_2 . This finding is quite surprising, since both EuFe_2P_2 and EuCo_2P_2 undergo pressure-induced structural ($\alpha \rightarrow \beta$) phase transition and reveal corresponding valence changes of Eu from Eu^{2+} to Eu^{3+} that results in a disappearance of the $\text{Eu}(4f)$ sublattice magnetism.

In order to illuminate this last point, we have performed volume-dependent linear muffin tin orbital (LMTO-47 Code¹⁵) band-structure calculations using density-functional theory in the local-density approximation (LDA) with the atomic spheres approximation (ASA).¹⁶ Experimental geometries (lattice parameters and atomic positions for α and β phases) were used throughout without further optimization. The ASA radii were calculated from Hartree potentials. Reciprocal space investigations were performed by the tetrahedron method¹⁷ using 436 irreducible κ points. The basis sets consisted of $6s/5d/4f$ for Eu, $4s/4p/3d$ for Fe and Co, and $3s/3p$ for P. The $6p$ orbitals of Eu and $3d$ -orbitals of P were “downfolded.”¹⁸ Spin-polarized calculations were made using the exchange correlation potential of von Barth and Hedin.¹⁹ All iterations converged to total energy changes smaller than 10^{-5} Rydberg.

The calculated densities of states (DOS) of EuFe_2P_2 and EuCo_2P_2 at ambient pressure (α phase) show typical patterns characteristic for ThCr_2Si_2 -type compounds.¹⁰ In the following we only focus on the Fe- and Co- $3d$ DOS in EuFe_2P_2 and EuCo_2P_2 , respectively.²⁰ In Figs. 4(a) and 4(b) we show the spin-polarized Fe- and Co- $3d$ DOS (sum of spin \uparrow and spin \downarrow) in the α phase of EuFe_2P_2 and EuCo_2P_2 , respectively.

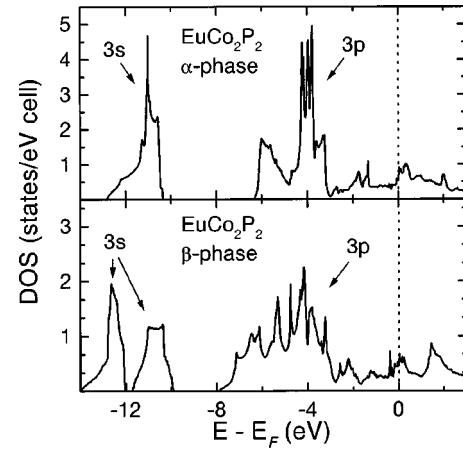


FIG. 5. Calculated P - $3p$ - and $3s$ -DOS in EuCo_2P_2 for the α and β phases.

As evident from this figure, a DOS-peak representing $dd\sigma^*$ antibonding states of metal $3d_{xy}$ orbitals¹⁰ is located above E_F at energies $\Delta E = E - E_F \approx 1.2$ eV for EuFe_2P_2 , but only 0.15 eV for EuCo_2P_2 due to one additional valence electron in the Co $3d$ shell. The analysis of these calculations reveal that neither Fe nor Co exhibit a $3d$ magnetic moment in these compounds. These results are in good agreement with those obtained experimentally.^{1,2}

Now, we discuss the $3d$ DOS for Fe and Co in EuFe_2P_2 and EuCo_2P_2 in the β phase. In EuFe_2P_2 [Fig. 4(a)] we find that the $\text{Fe}(3d)$ moment remains zero as in the α phase: In the β phase the filling of the $\text{Fe}(3d)$ band increases and consequently the Fe - $3d$ DOS gets closer to E_F ($\Delta E \sim 0.8$ eV). However, the $3d$ DOS at E_F remains rather low and no magnetic splitting takes place. This is consistent with our experimental observation of the absence of the Fe magnetic moment in the β phase of EuFe_2P_2 . On the other hand, in the β phase of EuCo_2P_2 the increase of $\text{Co}(3d)$ band filling results in a considerable enhancement of the DOS peak at E_F and a magnetic splitting takes place, which clearly indicates the formation of a Co magnetic moment. It is obvious that the proximity of the Co- $3d$ DOS-peak to E_F already at ambient pressure is the reason for a moment formation in the high-pressure phase of EuCo_2P_2 . The calculated magnetic moment for β - EuCo_2P_2 is found to be $0.66\mu_B/\text{Co}$ in a very good agreement with the estimated experimental value of $0.6\mu_B$.¹¹ These results raise an interesting question, whether the excess electrons for a d -band filling originates from the pressure-induced valence transition of Eu [$\text{Eu}^{2+}(4f^7) \rightarrow \text{Eu}^{3+}(4f^6)$] or the formation of the P-P bond ($2\text{P}^{3-} \rightarrow \text{P}_2^{4-}$). As shown in Fig. 5 our band-structure calculations show a strong reorganization of the P - $3p$ DOS when going from α to β phases, whereas the Eu levels (not shown) are not much affected. In fact, we find that the charge on the P site ($3p$ states) is lower in the β phase than the α phase which hints a transfer of electrons to fill the $3d$ band. This shows that the electronic transition from the nonbonding to the P-P single bond state is mainly responsible for the filling of the $3d$ states and thereby for the moment formation of Co in EuCo_2P_2 . This filling is not suf-

ficient to generate a moment on Fe in EuFe_2P_2 because of the lower valence electron count of Fe compared with Co.

In summary, our high-pressure results reveal that the pressure-induced structural phase transition in EuFe_2P_2 is connected with a continuous valence transition from magnetic Eu^{2+} to a nonmagnetic Eu^{3+} state. In contrast to EuCo_2P_2 , we find in the high-pressure phase of EuFe_2P_2 no magnetic moment on Fe. Volume-dependent band-structure

calculations on both systems show that the condition for the formation of the $3d$ moment strongly depends on the type of transition metal and the proximity of the $3d$ states relative to E_F . It is shown that the electronic transition from the non-bonding to the P-P single bond state is mainly responsible for the filling of the $3d$ states. We feel that our results would stimulate further experimental and theoretical efforts for a better understanding of pressure-induced magnetic and electronic phenomena in strongly correlated electron systems.

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- ¹M. Reehuis, W. Jeitschko, M. H. Möller, and P. J. Brown, *J. Phys. Chem. Solids* **53**, 687 (1992).
- ²E. Mörsen, B. D. Mosel, W. Müller-Warmuth, M. Reehuis, and W. Jeitschko, *J. Phys. Chem. Solids* **49**, 785 (1988).
- ³M. Reehuis, P. J. Brown, W. Jeitschko, M. H. Möller, and T. Vomhof, *J. Phys. Chem. Solids* **54**, 469 (1993).
- ⁴R. Nagarajan, E. V. Sampathkumaran, L. C. Gupta, and R. Vijayaraghavan, *Phys. Lett.* **84A**, 275 (1981).
- ⁵W. Jeitschko, R. Glaum, and L. Boonk, *J. Solid State Chem.* **69**, 93 (1987).
- ⁶R. Hoffman and C. Zhang, *J. Phys. Chem.* **89**, 4175 (1985), and references therein.
- ⁷A. Würth *et al.*, *Z. Anorg. Allg. Chem.* **623**, 1418 (1997).
- ⁸C. Huhnt *et al.*, *Physica B* **240**, 26 (1997).
- ⁹C. Huhnt, W. Schlabitz, A. Würth, A. Mewis, and M. Reehuis, *Phys. Rev. B* **56**, 13 796 (1997).
- ¹⁰D. Johrendt *et al.*, *J. Solid State Chem.* **130**, 254 (1997).
- ¹¹M. Chefki *et al.*, *Phys. Rev. Lett.* **80**, 802 (1998).
- ¹²C. Huhnt, W. Schlabitz, A. Würth, A. Mewis, and M. Reehuis, *Physica B* **252**, 44 (1998).
- ¹³W. Jeitschko, U. Meisen, and U. Scholz, *J. Solid State Chem.* **55**, 331 (1984).
- ¹⁴G. R. Hearne, M. Pasternak, and R. D. Taylor, *Rev. Sci. Instrum.* **65**, 3787 (1994).
- ¹⁵O. K. Andersen and O. Jepsen, *Tight-Binding LMTO* (Max-Planck-Institut für Festkörperforschung, Stuttgart, 1994).
- ¹⁶O. K. Andersen and O. Jepsen, *Z. Phys. B: Condens. Matter* **97**, 35 (1995).
- ¹⁷O. Jepsen and O. K. Andersen, *Solid State Commun.* **9**, 1763 (1971).
- ¹⁸W. R. L. Lambrecht and O. K. Andersen, *Phys. Rev. B* **34**, 2439 (1986).
- ¹⁹U. von Barth and L. Hedin, *J. Phys. C* **5**, 1629 (1972).
- ²⁰The extremely narrow Eu $4f$ bands are not accurately described by the LDA. A correct treatment would require a LDA+ U approach and the spin-orbit coupling. This has, however, no influence on the modification of the $3d$ states.