Pressure-induced Transition of the Sublattice Magnetization in $EuCo_2P_2$: Change from Local Moment $Eu(4f)$ to Itinerant $Co(3d)$ Magnetism

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(Received 19 August 1997)

Antiferromagnetism in $EuCo_2P_2$ ($ThCr_2Si_2$-type structure) is due to ordering of the $Eu^{2+}(^8S_{7/2})$ sublattice moments ($T_N = 66.5$ K) while the $Co(3d)$ sublattice does not carry any magnetic moment. $EuCo_2P_2$ undergoes a pressure-induced isostructural phase transition at $p_c = 3.1$ GPa. ^{151}Eu high-pressure Mössbauer experiments ($0 \leq p \leq 5$ GPa) reveal a valence transition of Eu from Eu^{2+} to nonmagnetic $Eu^{3+}(^7F_0)$ at $p > p_c$ with the consequence that the disappearance of the $Eu(4f)$ sublattice magnetism is accompanied by a simultaneous appearance of $Co(3d)$ sublattice magnetism ($T_N^* = 260$ K). The latter is explained by the filling of the $3d$ states. [S0031-9007(97)05140-5]

PACS numbers: 71.27.+a, 75.30.Kz, 76.80.+y

The rare earth (RE) transition metal (T) phosphides, RET_2P_2, which crystallize in the $ThCr_2Si_2$-type structure, show a broad spectrum in their magnetic properties. This spectrum covers the whole range from pure Pauli paramagnets (e.g., $LaFe_2P_2$ and $LaNi_2P_2$ [1]) to antiferromagnetically ordered compounds with two magnetic sublattices corresponding to ordered $4f$ and $3d$ moments, respectively (e.g., $PrCo_2P_2$ and $NdCo_2P_2$ [2]). In between, there are intermediate valent systems, such as $EuNi_2P_2$ [1,3] and $CeFe_2P_2$ [1], as well as antiferromagnetic ordered compounds wherein there are only $4f$ but *no* $3d$ moments (e.g., $EuCo_2P_2$ [4], $PrFe_2P_2$ [1]). The fact that the $T(3d)$ moment vanishes in some of the phosphides RET_2P_2 is a known feature of the $ThCr_2Si_2$-type structure. In $RET_2(Si,Ge)_2$, for example, the magnetic moments of all T elements are negligible, with $T =$ Mn being the only exception [5]. The recently discovered $RENi_2B_2C$ superconductors [6] again crystallize into a $ThCr_2Si_2$-type structure; the vanishing Ni moments in these compounds are the basis for the occurrence of superconductivity [7,8]. Thus, the investigation of the magnetic properties of the RET_2P_2 compounds, which crystallize in the $ThCr_2Si_2$-type structure, is a fundamental issue for a better understanding of $3d$ moment formation in these systems.

Another special aspect of the RET_2P_2 compounds is related to the fact that the lattice parameters of some compounds within this series differ considerably due to the existence of two extremely different P-P distances along the c axis: In some compounds there is a short P-P distance ($d_{\text{P-P}} \simeq 2.3$ Å) forming a P-P single bond state [9]; in others it is much larger ($d_{\text{P-P}} > 2.8$ Å), resulting in a negligible P-P bonding interaction (nonbonding P-P state). Structural phase transitions of first order between these two phases occur as a function of temperature (e.g., $EuRh_2P_2$ [10]), composition (e.g., $Eu(Rh_{1-x}Co_x)_2P_2$ [11]), or pressure (e.g., $EuCo_2P_2$ [12]). These "bonding" to "nonbonding" transitions should have a severe influence on the electronic structure and, consequently, on the $T(3d)$ magnetic moment formation, as pointed out in Ref. [13].

Regarding the above-mentioned aspects, $EuCo_2P_2$ is an excellent candidate for studying the effect of pressure on the electronic structure and the magnetism of the $Eu(4f)$ and $Co(3d)$ sublattice, respectively, and their mutual relationship. At ambient pressure, $EuCo_2P_2$ shows antiferromagnetic (AF) order of the $EU^{2+}(^8S_{7/2})$ moments below $T_N = 66.5$ K. According to neutron scattering studies [4], the AF structure consists of layers of ferromagnetically coupled Eu^{2+} moments in the a-b plane, which are twisted against each other in such a way that they form an incommensurate spiral structure with the c axis as the spiral axis. The Co sublattice does *not* participate in the magnetic ordering, i.e., Co carries no magnetic moment in this compound. The pressure effect on the *structure* of $EuCo_2P_2$ has been demonstrated very recently by our group: With increasing pressure it undergoes a first order structural phase transition at about $p_c \simeq 3.1$ GPa from the nonbonding to the bonding P-P state [12]. The lattice parameters obtained for the high-pressure phase of $EuCo_2P_2$ ($p > 3.1$ GPa) indicate that this structural phase transition may be connected with a change of the Eu valence from Eu^{2+} towards a Eu^{3+} state.

For the reasons given above, we have performed ^{151}Eu high-pressure Mössbauer effect (ME) experiments on $EuCo_2P_2$. Using the high-pressure ME technique, one can simultaneously study the possible pressure-induced change of the Eu valence ($Eu^{2+} \rightarrow Eu^{3+}$) *and* the corresponding change from the $Eu^{2+}(^8S_{7/2})$ magnetic state to a nonmagnetic state [$Eu^{3+}(^7F_0)$ has no magnetic moment]. Furthermore, one can investigate whether such a change of the unit cell volume and/or the electronic structure at the structural phase transition affects the Co($3d$) sublattice magnetism in this compound.

Our results reveal that the structural phase transition in $EuCo_2P_2$ at $p_c \simeq 3.1$ GPa is accompanied by a valence transition from Eu^{2+} to Eu^{3+} with severe consequences on the nature of the magnetism in this compound: We find a change from a local $Eu^{2+}(^8S_{7/2})$ sublattice magnetism to a magnetically ordered state ($T_N^* \simeq 260$ K), where only the Co sublattice is carrying a magnetic moment ($\mu_{Co} \simeq 0.6\mu_B$). Such a pressure-induced change of the sublattice magnetism from local $4f$ to itinerant $3d$ has, up to now, not been observed in any RE($4f$)-T($3d$) magnetic system and provides an excellent basis for testing band structure calculations of $3d$ magnetic moment formation in the $ThCr_2Si_2$-type structure.

For a detailed description of the synthesis and characterization of $EuCo_2P_2$ (purity of starting materials, chemical stability, etc.), see Ref. [14]. The high-pressure ME setup using B_4C anvils is described elsewhere [15]. Both source ($^{151}SmF_3$, $\simeq$100 mCi) and absorber were kept at the same temperature in a variable temperature He cryostat.

Figure 1 shows the pressure dependence of the unit cell volume of $EuCo_2P_2$ for pressures up to $\simeq$5 GPa as obtained by energy dispersive powder diffraction spectra, which were acquired at the Hamburger Synchrotron Strahlungslabor (HASYLAB), beam line F2/1, by using the Multianvil x-ray device (MAX80). The structural phase transition of first order can be seen clearly with increasing pressure ($p_c \simeq 3.1$ GPa) as well as with decreasing pressure ($p_c^* \simeq 1.9$ GPa), indicating that the phase transition is fully reversible. The volume collapse ($\frac{\Delta V}{V} \simeq -8\%$) is due only to an extreme decrease of the c axis, whereas the lattice parameter a even *increases* at the phase transition with increasing pressure (see below).

The ^{151}Eu ME spectra taken at 300 K at ambient pressure, $p = 3.3$ GPa (well below and just above the structural phase transition), and after releasing pressure are shown in Fig. 2. The center shift of the ^{151}Eu resonance line changes dramatically from $S = -10.62(4)$ mm/s at ambient pressure to $S = -2.91(5)$ mm/s at $p = 3.3$ GPa. This indicates clearly that, at the structural phase transition, Eu changes its valence state from Eu^{2+} at ambient pressure to Eu^{3+} (or an intermediate valence state) at $p = 3.3$ GPa. The ^{151}Eu ME spectra collected at 4.2 K at ambient pressure and at 5 GPa, i.e., well above the structural phase transition, are shown in Fig. 3. At ambient pressure ($T = 4.2$ K) we find, as expected, a magnetically split Eu^{2+} spectrum which is due to the ordering of the $Eu^{2+}(^8S_{7/2})$ moments below T_N. The value of the effective magnetic hyperfine (hf) field $B_{\rm eff}$ [$B_{\rm eff} = 26.00(6)$ T] at the $^{151}Eu^{2+}$ nuclei and the center shift are in good agreement with already published data [2]. At 5 GPa and $T = 4.2$ K (Fig. 3) we observe a complex ME spectrum which indicates the existence of a magnetically ordered state: It consists of two components, a single Eu^{3+} line ($\simeq$37% of the total absorption area) and a magnetically ordered spectrum ($\simeq$63% of the total absorption area), both having the *same* center shift, i.e., the same valence (Eu^{3+}) state. The observation of a magnetic hf field [29.3(6) T] at a nonmagnetic $Eu^{3+}(^7F_0)$ state is quite surprising. The only explanation is that this hf field is an *induced*

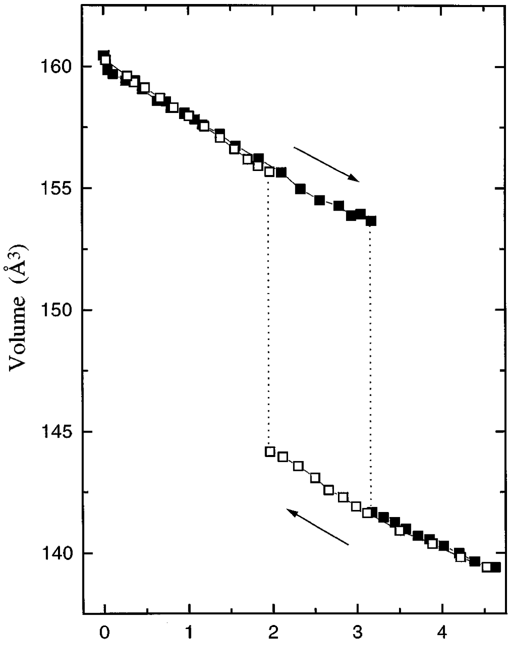

FIG. 1. Pressure dependence of the unit cell volume of $EuCo_2P_2$ as obtained from high-pressure x-ray diffraction measurements at 300 K. The isostructural first order transition occurs at $p_c \simeq 3.1$ GPa and $p_c^* \simeq 1.9$ GPa upon applying and releasing pressure, respectively.

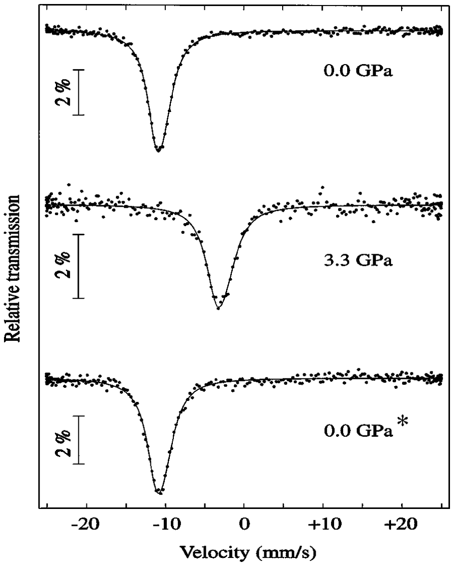

FIG. 2. ^{151}Eu Mössbauer spectra of $EuCo_2P_2$ ($T = 300$ K) at ambient pressure, $p = 3.3$ GPa, and after releasing pressure ($*$).

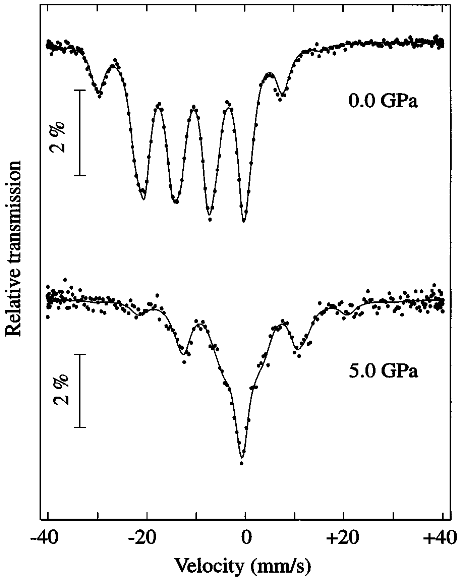

FIG. 3. ^{151}Eu Mössbauer spectra of $EuCo_2P_2$ ($T = 4.2$ K) at ambient pressure and at $p = 5$ GPa. The magnetically hf split spectrum at $p = 0$ GPa [$S = -10.62(4)$ mm/s] corresponds to the Eu^{2+} state, whereas that at $p = 5$ GPa corresponds to the Eu^{3+} state which is centered at $S = -0.82(5)$ mm/s.

magnetic hf field (B_{ind}) which results from ordered Co($3d$) moments. Its origin is due either to the spin polarization of the conduction electrons by the Co moment and/or to the admixture of excited Eu^{3+} states (e.g., $^7F_1$) into the ground state (($^7F_0$) by the Co-Eu exchange field [16]. The fact that a part of the Eu^{3+} nuclei ($\simeq$37%) exhibits no B_{ind} gives information on the magnetic structure of the Co($3d$) moments (see below).

In order to determine the magnetic ordering temperature of the Co($3d$) sublattice magnetization, we have measured the temperature dependence of the ^{151}Eu ME spectrum in the high-pressure phase. By analyzing these data we obtained the temperature dependence of the induced hf field, which is shown in Fig. 4. A magnetic ordering temperature $T_N^* = 260 \pm 6$ K can be extrapolated from this figure. This value is much higher than that of $T_N = 66.5$ K resulting from the Eu^{2+} moments at ambient pressure, but is comparable with those obtained for other $RE^{3+}Co_2P_2$ compounds where the Co($3d$) moments are responsible for the occurrence of magnetic order (e.g., $PrCo_2P_2$: $T_N^* = 304$ K; $NdCo_2P_2$: $T_N^* = 309$ K [1]). This result provides further support that the nature of the magnetic ground state is essentially different in the high- and low-pressure phases of $EuCo_2P_2$. To our knowledge, this is the first time that a pressure-induced change of the sublattice magnetization from pure RE($4f$) to $T(3d)$ is observed in a RE-T magnetic system.

Before discussing the appearance of Co($3d$) moments in the high-pressure phase of $EuCo_2P_2$, we would like to mention here that all pressure-induced changes are reversible upon releasing pressure (see Fig. 2). The reason why our observation is against the common intuition is the fact that usually high pressure is known to reduce $3d$ magnetic moments due to a reduction of the density of states. Further discussion will explain the appearance of Co($3d$) moments in the high-pressure phase of $EuCo_2P_2$. The high-pressure phase of $EuCo_2P_2$ differs both in the crystallographic and in the electronic structure from the low-pressure phase. The changes of the lattice parameters at p_c are the following: (i) extreme decrease of the lattice parameter c ($\Delta c/c \simeq -13\%$) and (ii) increase of a ($\Delta a/a \simeq +3\%$). Consequently, the changes of the electronic structure are quite severe: first, a transition from a nonbonding to a P-P single bond state, i.e., from $2(P^{-3})$ to ${P_2}^{-4}$, which results in a change of the Co formal charge (oxidation state) from +2.0 to +1.0 and, second, an Eu valence transition from a Eu^{2+} to a Eu^{3+} state, which gives an additional change of the Co formal charge from +1.0 to +0.5. The changing charge at the Co site—decreasing from +2.0 to +0.5—results in an increase in the number of Co($3d$) conduction electrons, i.e., in a filling of the Co($3d$) band. Very recently, band structure calculations performed on $ThCr_2Si_2$-type compounds [17] have shown that such a strong connection between P-P bonding and d-shell filling indeed exists. If this Co($3d$) band filling shifts the Fermi energy (E_F) to a position with a higher density of states $D(3d)$, we can explain both the formation of a Co($3d$) moment and the relatively high magnetic ordering temperature. On the basis of the data analysis made in Ref. [13] with respect to Co($3d$) magnetic moment formation in the $ThCr_2Si_2$-type phosphides, we estimate the Co($3d$) moment to be about 0.6 μ_B in the high-pressure phase of $EuCo_2P_2$. In this respect, we want to mention that the anisotropic pressure-induced change of the lattice parameters at p_c additionally supports the Co($3d$)-moment formation: An increase of the lattice parameter a at p_c (see above) results from increasing distances

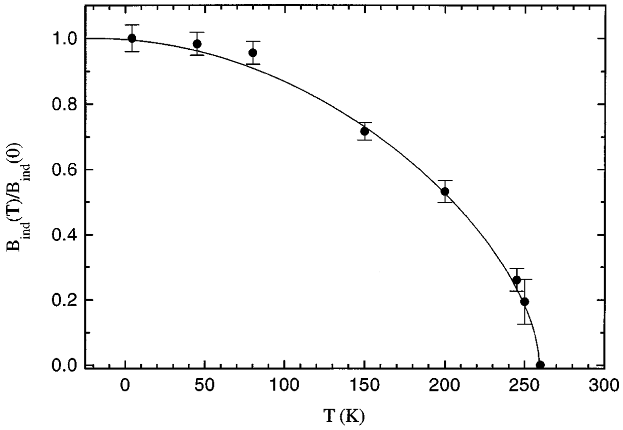

FIG. 4. Temperature dependence of the induced magnetic hf field (B_{ind}) normalized to its value at 4.2 K [$B_{\text{ind}}(0)$] as obtained from the magnetically split spectra at 5 GPa. The line through the data points is a guide to the eye.

from Co to its nearest neighbors ($\Delta d_{\text{Co-Co}}/d_{\text{Co-Co}} = \Delta a/a \simeq +3\%$; $\Delta d_{\text{Co-P}}/d_{\text{Co-P}} \simeq +2\%$). Such an increase in $d_{\text{Co-Co}}$ and $d_{\text{Co-P}}$, respectively, will certainly reduce the $3d$ bandwidth and thus will additionally increase $D(3d)$ at E_F.

Finally, we discuss the possible magnetic structure of the Co moments in the high-pressure phase which leads to the observation that part ($\simeq$37%) of the Eu^{3+} nuclei does not see any induced magnetic hf field. Recent neutron diffraction studies of the magnetic order in the $ThCr_2Si_2$-type phosphides $Pr^{3+}Co_2P_2$ and $Nd^{3+}Co_2P_2$ [18] revealed that the Co moments order along the c axis with ferromagnetic order within the basal planes and *antiferromagnetic* order between these planes. The stacking sequence of the antiferromagnetic order is $+ + - -$, $+ + - -$, and results in two magnetically *inequivalent* RE sites: one (site "*A*") having all of its eight Co nearest-neighbor moments parallel to each other and the other one (site "*B*") having these eight Co moments antiparallelly ordered (four up and four down). Thus, site *A* will have an induced magnetic hf field while B_{ind} will be zero at site *B*. If we assume that the high-pressure phase of $EuCo_2P_2$ has the same order of Co moments as that of $PrCo_2P_2$ and $NdCo_2P_2$, respectively, we would expect that 50% of the Eu^{3+} nuclei will have $B_{\text{ind}} = 0$. The experimental observation that only 37(2)% of the Eu^{3+} nuclei have $B_{\text{ind}} = 0$ clearly requires a different stacking sequence, namely, $+ + + - - -$, $+ + + - - -$. In this case, the theoretical ratio for the site occupation (site$'$ A'/site$'$ B') = 2.0 is very close to the experimental value (site$'$ A'/site$'$ B') = 1.7(0.2). The small difference between the experimental and theoretical value can be explained by stacking faults. For an exact determination of the magnetic structure of the Co sublattice, high-pressure neutron diffraction experiments on $EuCo_2P_2$ are highly desired.

In conclusion, our experimental results reveal a unique feature of the $EuCo_2P_2$ system: Depending on its lattice parameters, it completely changes its magnetic character from a pure Eu($4f$)- to a Co($3d$)-sublattice magnetism. This compound, therefore, can be used as a model system for band structure calculations in connection with the actual problem of $3d$ moment formation in the $ThCr_2Si_2$-type structure.

The authors would like to thank J.P. Sanchez and D. Khomskii for useful discussions. Thanks are also due to Th. Peun and P. Zinn for their valuable advice throughout the course of experiments at MAX 80 (HASYLAB, beam line F2/1).

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