

First-order phase transitions in EuCo_2P_2 and SrNi_2P_2

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First-order phase transitions with strong and extremely anisotropic changes of the lattice parameters were observed in the ThCr_2Si_2 structure-type compounds EuCo_2P_2 and SrNi_2P_2 . At room temperature, with increasing pressure the phase transition occurs in SrNi_2P_2 at 4 kbar and in EuCo_2P_2 at 30 kbar which is in the latter probably accompanied by a valence change of Eu. On the basis of single-crystal data of ACo_2P_2 ($A = \text{Ca, Sr, La, Ce, Pr, Nd, Eu}$) at ambient pressure and temperature we discuss the pressure dependence of the bond lengths in these compounds. [S0163-1829(97)00346-9]

I. INTRODUCTION

With more than 700 different compounds the ThCr_2Si_2 structure type exhibits the most representatives.¹ The body-centered-tetragonal ThCr_2Si_2 structure of AT_2X_2 stoichiometry ($A =$ alkaline-earth or rare-earth element; $T =$ transition metal, $X = \text{B, P, Si, As, Ge}$), which is shown in Fig. 1 for $X = \text{P}$, has only one crystallographic site for each atomic species and one variable parameter z_X which determines the relative position of X within the unit cell. Essentially responsible for the large number of different representatives is the possibility of this structure type to adapt to strongly different atomic sizes leading to the occurrence of extremely different lattice parameters.

Among the phosphides especially the shortest P-P distance $d_{\text{P-P}}$ with the connection line parallel to the c axis (Fig. 1) can be strikingly changed even by replacing one element by another of similar size: it changes from 3.284 Å in SrRh_2P_2 (Ref. 2) and 3.273 Å in EuCo_2P_2 ,³ respectively, which is in both cases too long for any covalent P-P bond, to 2.217 Å in SrPd_2P_2 (Ref. 4) and 2.371 Å in EuNi_2P_2 ,⁵ respectively, which is within the range of a P-P single bond.⁶ Indeed, in the framework of band-structure calculations this extreme change of the P-P distance was explained by a transition of a P-P state without any bond to a P-P single bond state.^{6,7} In a recent publication⁸ we showed that this transition is of first order and can be induced either by applying external pressure (at 6 GPa in SrRh_2P_2) or temperature (at 800 K in EuRh_2P_2). In the latter compound it is accompanied by a valence change of Eu. We supposed that this transition should be not only restricted to the Rh phosphides, but also be observable in those phosphides containing $3d$ transition metals, particularly in EuCo_2P_2 . In order to investigate the structural properties of these compounds, we performed measurements of the lattice parameters as function of pressure and temperature on ACo_2P_2 ($A = \text{Ca, Sr, La, Ce, Pr, Nd, Eu}$) and on ANi_2P_2 ($A = \text{Ca, Sr, Tb, Dy, Er}$).

II. EXPERIMENT

The measurements of the lattice constants as function of pressure at 300 and 750 K were performed by energy-dispersive x-ray diffraction on powdered samples using the Multi Anvil x-ray device (MAX 80) at the Hamburger Synchrotron Strahlungslabor (HASYLAB), beamline F2/1. The temperature-dependent x-ray diffraction measurements were performed by using $\text{Cu } K\alpha$ radiation with a Siemens D5000 diffractometer in Bragg Brentano geometry.

For a detailed description of the synthesis and characterization of the compounds (purity of starting materials, chemical stability, etc.) see Refs. 3, 5, 9 and 10.

III. RESULTS ON EuCo_2P_2

The x-ray-diffraction measurements were performed on two different samples of EuCo_2P_2 . In the first sample (sample 1), which was studied in more detail, an impurity phase of about 4% — containing according to ¹⁵¹Eu Moessbauer measurements trivalent Eu (Ref. 11) — was observed. The results of sample 1 were confirmed later by measurements on a second sample (sample 2), which was free of impurities.

The energy-dispersive x-ray powder-diffraction spectra of EuCo_2P_2 (sample 2) at 300 K for different pressures are shown in Fig. 2. At standard temperature and pressure (stp) all observed peaks (lowest x-ray pattern of Fig. 2) except those of the Eu- K fluorescence lines can be identified with the ThCr_2Si_2 structure type and with lattice parameters which correspond within the accuracy of measurement to those of EuCo_2P_2 given by literature.³ Above 27 kbar new peaks arise in the spectra which are rapidly increasing in intensity with increasing pressure on the expense of the old peaks. The observed first-order phase transition is completed at pressures above 40 kbar and the peaks of the corresponding spectra (top of Fig. 2) can be also all identified with the

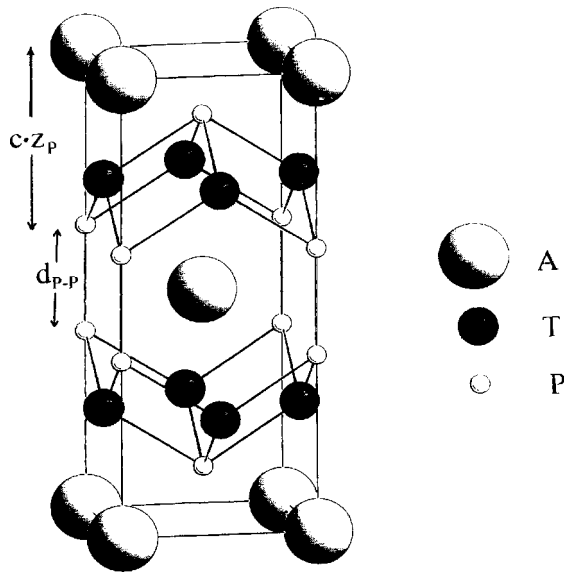


FIG. 1. The ThCr_2Si_2 structure type of AT_2P_2 stoichiometry. The relative position of P within the unit cell is given by the dimensionless parameter z_p .

ThCr_2Si_2 type. The peak energies of this new high-pressure phase of EuCo_2P_2 correspond to lattice parameters which are extremely changed compared to those of the low-pressure phase below 30 kbar.

The determined lattice constants of EuCo_2P_2 (sample 2) are shown in Fig. 3 versus pressure together with those found for $A\text{Co}_2\text{P}_2$ containing alkaline-earth elements $A = \text{Ca}, \text{Sr}$ or the rare-earth elements $A = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}$. Indeed, at the first-order phase transition at 31 kbar the lattice parameters of EuCo_2P_2 which are listed in Table I change extremely: while the c axis is reduced from 11.006 to 9.651 Å (−12.3%) the a axis even increases from 3.750 to 3.856 Å (+2.8%) leading to an extreme collapse of the c/a ratio (−14.7%) (see Table I). The lattice parameters of the low-pressure phase of EuCo_2P_2 ($p < 31$ kbar) are similar to those of SrCo_2P_2 and LaCo_2P_2 : rather long c axis ($c > 10.5$ Å), short a axis ($a < 3.81$ Å), and a high c/a ratio ($c/a > 2.8$). The compressibilities of these compounds (listed in Table II) are very anisotropic ($\kappa_c/\kappa_a > 2$). Contrarily, the lattice constants of the high-pressure phase of EuCo_2P_2 ($p > 31$ kbar) resemble those of $A\text{Co}_2\text{P}_2$ with $A = \text{Ca}$ or the rare-earth elements $\text{Ce}, \text{Pr},$ or Nd : short c axis ($c < 9.8$ Å), long a axis, and a c/a ratio in the vicinity of $c/a = 2.5$. Compared to the former compounds the compressibilities of the latter ones ($p > 20$ kbar for PrCo_2P_2) are rather isotropic ($\kappa_c/\kappa_a \approx 1.6$, see Table II). Among these compounds a significantly more anisotropic compression is observed only in PrCo_2P_2 below 20 kbar ($\kappa_c/\kappa_a \approx 2.5$).

The structural phase transition occurring in sample 1 of EuCo_2P_2 was measured in more detail (Fig. 4). The results of sample 1 are consistent with those found for sample 2. As function of pressure we observe at 300 an enormous hysteresis with the width $\Delta p = 12$ kbar: while the phase transition occurs also at 31 kbar with increasing pressure it occurs at about 19 kbar with decreasing pressure. At 750 K the hysteresis is strongly reduced ($\Delta p = 5$ kbar): the lower transition pressure significantly increases to about 25 kbar whereas the upper one even slightly decreases to about 30 kbar.

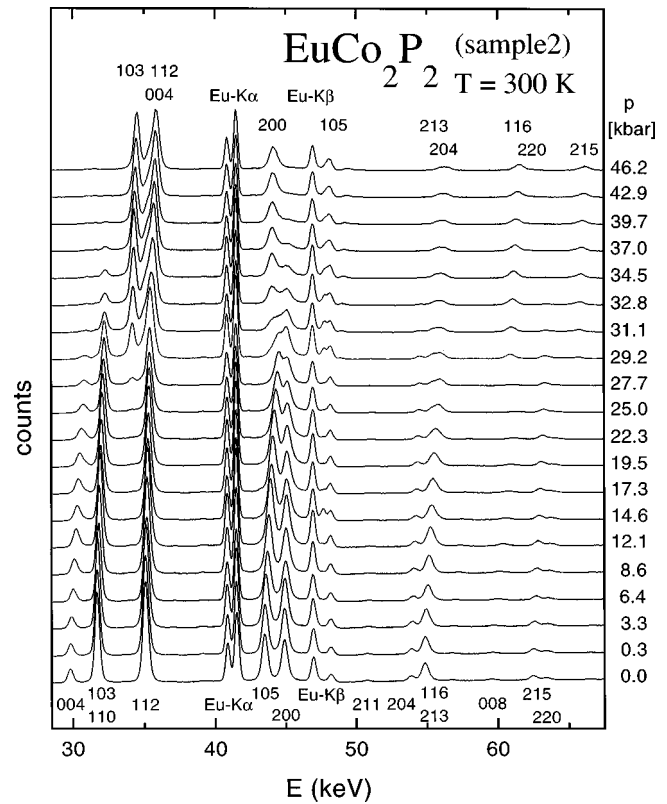


FIG. 2. X-ray-diffraction pattern of EuCo_2P_2 (sample 2) at different pressure values. At the first-order phase transition (at about 31 kbar) new peaks of the high-pressure phase arise at the expense of those of the low-pressure phase.

While the changes of the lattice parameters at the phase transition at 300 K are nearly the same as those of sample 2 (see above and Table I) they are strongly reduced to $\Delta a = +0.07$ Å (+1.9%) and $\Delta c = -0.97$ Å (−8.9%) at 750 K. Hence, the changes of the lattice parameters at the phase transition at 750 K make up only about 70% of those at 300 K. Only the ratio $\Delta c/\Delta a$ remains at both temperatures nearly the same ($\Delta c/\Delta a \approx 4.7$).

The change of the lattice constants is quite different in the high- and low-pressure phases of EuCo_2P_2 also as function of temperature: Contrary to the increase of the c/a ratio in the high-pressure phase with increasing temperature (300–750 K), c/a strongly decreases in the low-pressure phase (see Fig. 4). Consistent with this observation are the results of x-ray-diffraction measurements at ambient pressure as function of temperature on $A\text{Co}_2\text{P}_2$ ($A = \text{Sr}, \text{Pr}, \text{Nd}, \text{Eu}$) shown in Fig. 5. Concerning the temperature dependence of the lattice constants in this series we can again distinguish two kinds of compounds (see Table III). The thermal expansion α_c along c is in the compounds with long c axis (note the axis breaks in Fig. 5), i.e., SrCo_2P_2 and EuCo_2P_2 (sample 1), very small whereas it is along a in the order of $\alpha_a \approx 2 \times 10^{-5}/\text{K}$. This leads to a linear decrease of c/a as function of temperature. In sharp contrast the c axis of the compounds with short c axis, i.e., PrCo_2P_2 and NdCo_2P_2 , increases strongly with increasing temperature whereas a depends only weakly on temperature. Hence, the c/a ratio strongly increases with increasing temperature. In PrCo_2P_2 the lattice parameters depend linearly on tempera-

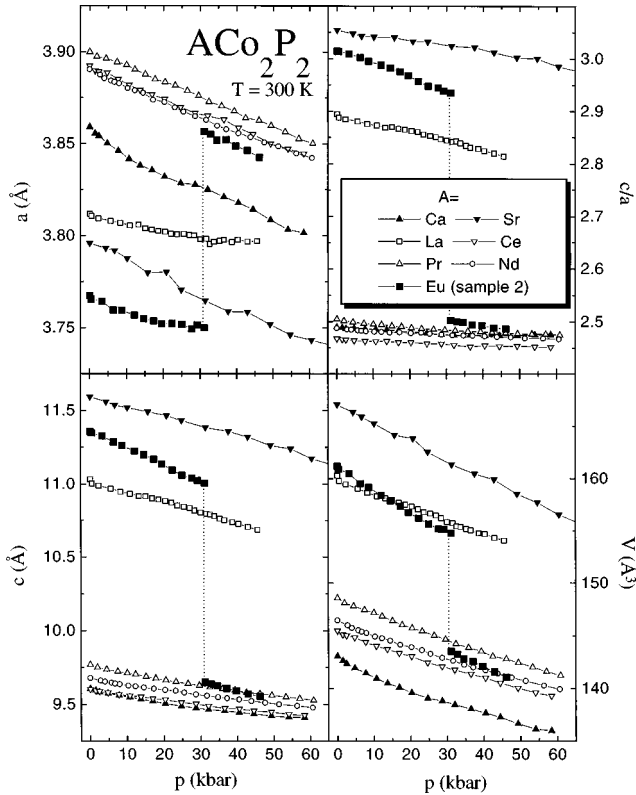


FIG. 3. Lattice parameter of ACo_2P_2 [$A = \text{Ca}, \text{Sr}, \text{La}, \text{Pr}, \text{Nd}, \text{Eu}$ (sample 2)] as function of pressure.

ture in the temperature range between 400 and 600 K only, but the thermal expansion is especially in this temperature range very large and extremely anisotropic [$\alpha_c \approx 1 \times 10^{-4}/\text{K}$ (!), $\alpha_a \approx -5 \times 10^{-6}/\text{K}$ (see Table III)].

Figure 6 shows the volume of all measured compounds of ACo_2P_2 stoichiometry at ambient pressure (top) and determined from the measured data for $p = 40$ kbar (middle) as function of the ionic radii given by Iandelli and Palenzona¹² for divalent alkaline-earth elements and for trivalent rare-earth elements. Except for EuCo_2P_2 and CeCo_2P_2 one observes for both pressure values a rather linear dependence of the volume on the ionic radius given by the straight lines in Fig. 6. While the deviation from these lines in the case of CeCo_2P_2 is due to intermediate valency¹³ it is in the case of EuCo_2P_2 — at ambient pressure — due to the divalent Eu atom.³ At 40 kbar the deviation for EuCo_2P_2 from the straight line is strongly reduced ($\approx 3 \text{ \AA}^3$) and it is even less than the corresponding deviation of intermediate valent EuNi_2P_2 ($\approx 4 \text{ \AA}^3$) from the other compounds of ANi_2P_2 stoichiometry containing trivalent rare-earth elements¹⁴ [Fig. 6 (bottom)]. Hence, from the structural point of view there is strong evidence for a valence change in EuCo_2P_2 at the phase transition with increasing pressure from Eu^{2+} to a trivalent or intermediate valent Eu state.

IV. RESULTS ON SrNi_2P_2

A further striking result was observed in SrNi_2P_2 . Before describing it in detail we note the following: Just recently,¹⁵ with structure refinements on the basis of x-ray single-crystal data it was shown that SrNi_2P_2 at ambient pressure and

TABLE I. Change of the lattice parameters at the phase transitions occurring in EuCo_2P_2 and SrNi_2P_2 .

	EuCo_2P_2		SrNi_2P_2	
	Sample 2	Sample 1	Sample 1	Sample 1
T (K)	300	300	750	300
p (kbar)	31	31	30	4
a (\AA)	LP phase	3.750	3.739	3.783
	HP phase	3.856	3.839	3.853
Rel. diff. (%)	+2.8	+2.7	+1.9	+1.3 ^a
c (\AA)	LP phase	11.006	10.992	10.837
	HP phase	9.651	9.623	9.866
Rel. diff. (%)	-12.3	-12.4	-9.0	-6.3
c/a	LP phase	2.935	2.939	2.865
	HP phase	2.503	2.507	2.561
Rel. diff. (%)	-14.7	-14.7	-10.6	-8.0
V (\AA^3)	LP phase	154.77	153.69	155.10
	HP phase	143.51	141.79	146.50
Rel. diff. (%)	-7.3	-7.7	-5.5	-3.9
$\Delta c/\Delta a$	4.4	4.7	4.8	4.9

^aDue to the superstructure in SrNi_2P_2 at stp the a axis is trebled (for further explanation see text).

temperature crystallizes in a superstructure of the ThCr_2Si_2 type caused by a displacement of the atoms from their ideal position. This leads to a trebling of the unit cell according to $b=3a$ and is not visible in x-ray powder-diffraction spectra. Hence, in order to determine pressure-dependent lattice parameters of SrNi_2P_2 from the present data we assumed an undistorted ThCr_2Si_2 structure type.

Similar to EuCo_2P_2 a first-order phase transition with hysteresis occurs in SrNi_2P_2 at 4 kbar with increasing pressure and at about 1 kbar with decreasing pressure, respectively (Fig. 7). Again the c axis at the phase transition strongly decreases (-6.3%) whereas the a axis increases ($+1.3\%$). The changes of the lattice parameters make up only about the half than those observed in EuCo_2P_2 , but the anisotropy of the lattice change in SrNi_2P_2 ($\Delta c/\Delta a \approx 4.9$) is nearly the same as that observed in EuCo_2P_2 (see above and Table I). The compression is again much more anisotropic in the low-pressure phase of SrNi_2P_2 ($\kappa_c/\kappa_a \approx 7$) than in the high-pressure phase [$\kappa_c/\kappa_a \approx 3$ ($p < 15$ kbar)] especially at higher pressures [$\kappa_c/\kappa_a \approx 2$ ($15 \text{ kbar} < p < 50 \text{ kbar}$)].

The lattice parameters determined for ANi_2P_2 ($A=\text{Ca}, \text{Tb}, \text{Dy}, \text{Er}$) as a function of pressure are shown in Fig. 8 together with those of SrNi_2P_2 . Contrary to the compression of SrNi_2P_2 in these compounds it is rather isotropic: the c/a ratio increases only slightly with increasing pressure and the c/a ratio of all compounds is (for $p > 4$ kbar) almost the same ($c/a \approx 2.4$). At 45 kbar it is correlated with

TABLE II. Compressibilities of the ThCr_2Si_2 type phosphides containing Co or Ni at 300 K (sample 2 of EuCo_2P_2). The compressibilities κ_i ($I=a,c,V$) were obtained by a linear fit to the data between the given pressure values p_1 and p_2 by using $\kappa_i = -[1/I(p_1)](\Delta I/\Delta p)$.

Compound	Pressure range	$\kappa_a(10^{-4}/\text{kbar})$	$\kappa_c(10^{-4}/\text{kbar})$	$\kappa_V(10^{-4}/\text{kbar})$	κ_c/κ_a
CaCo_2P_2	0 – 50 kbar	2.4(1)	3.9(1)	8.7(3)	1.6
CeCo_2P_2	0 – 50 kbar	2.11(4)	3.29(7)	7.4(1)	1.6
SrCo_2P_2	0 – 50 kbar	2.5(1)	5.5(1)	10.3(2)	2.2
LaCo_2P_2	0 – 50 kbar	0.93(5)	6.5(1)	8.3(1)	7.3
PrCo_2P_2	0 – 20 kbar	2.05(9)	5.1(1)	9.1(3)	2.5
PrCo_2P_2	20 – 50 kbar	2.16(5)	3.68(7)	7.9(2)	1.7
NdCo_2P_2	0 – 50 kbar	2.14(2)	3.46(7)	7.7(1)	1.6
EuCo_2P_2 (LP phase)	0 – 30 kbar	1.6(1)	10.2(2)	13.4(2)	6.3
EuCo_2P_2 (HP phase)	30 – 45 kbar	3.0(1)	4.7(4)	10.6(4)	1.5
CaNi_2P_2	0 – 45 kbar	3.33(9)	2.76(8)	9.3(2)	0.8
SrNi_2P_2 (LP phase)	0 – 4 kbar	2.1(2)	15.1(6)	19.3(6)	7.2
SrNi_2P_2 (HP phase)	5 – 15 kbar	3.2(1)	9.1(8)	15.5(7)	2.8
SrNi_2P_2 (HP phase)	15 – 50 kbar	2.6(1)	5.2(2)	10.4(1)	2.0
TbNi_2P_2	0 – 50 kbar	2.78(6)	2.12(6)	7.6(2)	0.8
DyNi_2P_2	0 – 45 kbar	2.6(1)	2.3(1)	7.4(2)	0.9
ErNi_2P_2	0 – 50 kbar	2.56(7)	1.57(6)	6.6(2)	0.6

the valence of the A atom: The c/a ratio of the compounds containing the divalent alkaline-earth elements $A = \text{Ca}, \text{Sr}$ is smaller than those of ANi_2P_2 containing the trivalent rare-earth elements $\text{Tb}, \text{Dy},$ or Er .

In contrast to the other compounds of ANi_2P_2 stoichiometry the compressibility of SrNi_2P_2 which is the highest in this series, significantly decreases with increasing pressure (Table II). A reason for that is given in the Discussion.

V. DISCUSSION

A precise determination of the bond lengths from phosphorus to its neighboring atoms from the present data is unfortunately not possible, because the unknown relative position of phosphorus within the unit cell, which is given by the dimensionless parameter z_p (shown in Fig. 1), was not directly measurable. Fortunately, it is possible to perform meaningful estimates basing on the following arguments: In the AT_2P_2 compounds containing the $3d$ transition-metal elements $T = \text{Fe}, \text{Co},$ or Ni z_p depends rather linearly on the c/a ratio (Fig. 9).¹ A similar dependence also exists in the AT_2P_2 compounds containing $4d$ transition-metal elements $T = \text{Ru}$ and Rh (Ref. 1) and was in the case of ARh_2P_2 compounds already used for an estimation of the bond lengths as function of pressure and temperature.⁸ Hence, in order to describe the behavior of these bond lengths in ACo_2P_2 we also assumed that this linear dependence of z_p on c/a holds as function of pressure and temperature. Particularly for the compounds containing Fe or Co

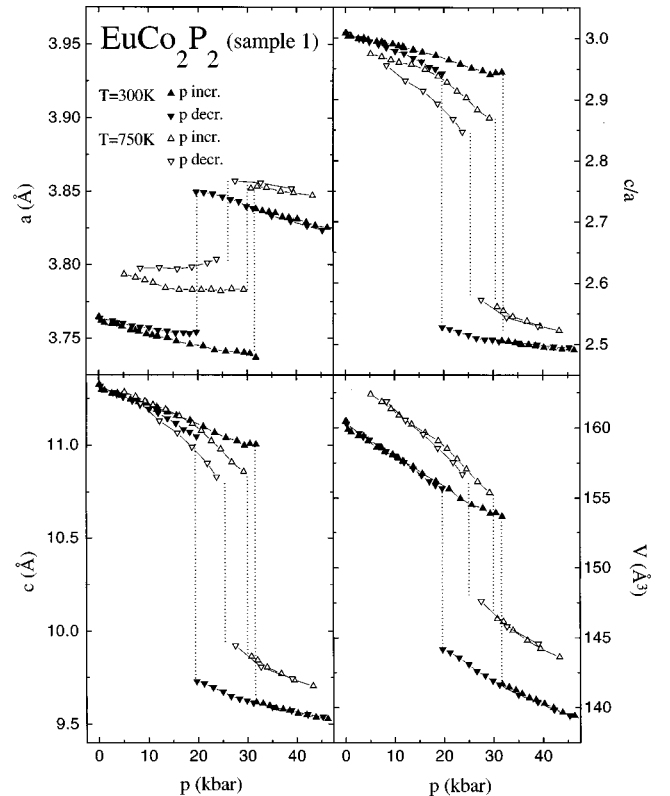


FIG. 4. Lattice parameter of EuCo_2P_2 (sample 1) at 300 and at 750 K as function of pressure.

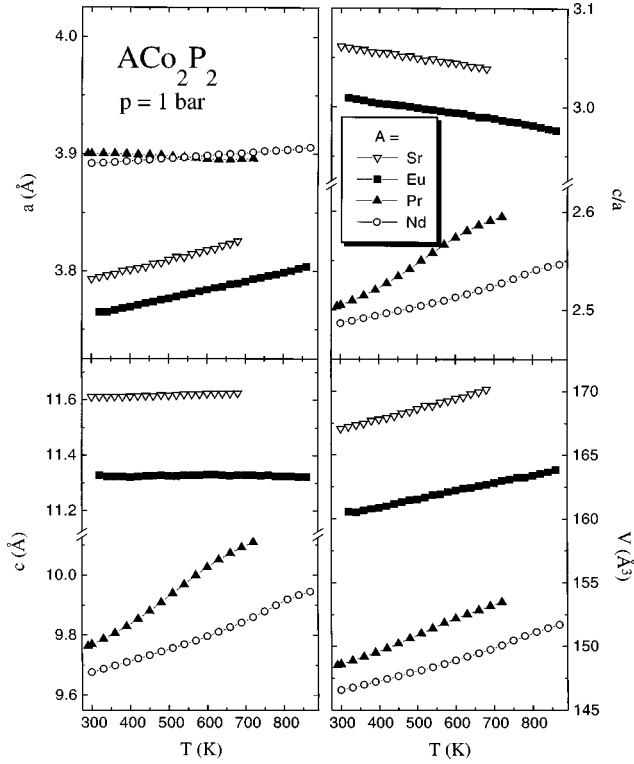


FIG. 5. Lattice parameter of ACo_2P_2 [$A = Sr, Pr, Nd, Eu$ (sample 1)] as function of temperature.

the deviations from the linearity given by the straight line in Fig. 9 are (at ambient pressure and temperature) rather small ($\Delta z_p < 0.003$). This deviation would cause a significant error of estimation only in the case of the distance d_{P-P} of the phosphorus atoms perpendicular to the layers ($\Delta d_{P-P} < 0.06 \text{ \AA}$), but not even this will affect the conclusions.

The bond lengths d_{P-P} , d_{Co-P} , d_{A-P} and d_{A-Co} of the ACo_2P_2 compounds, which were calculated in this way, are shown in Fig. 10(a) as function of pressure and in Fig. 10(b) as function of temperature. At the phase transition in $EuCo_2P_2$ at 31 kbar especially the P-P distance changes with increasing pressure dramatically from about 3.153 \AA to about 2.511 \AA ($\Delta d_{P-P} = -20.4\%$), but also the bond lengths from the Eu to its nearest neighbors are strongly reduced ($\Delta d_{Eu-P} = -2.7\%$, $\Delta d_{Eu-Co} = -7.2\%$). The length of the covalent Co-P bond even increases at the phase transition with

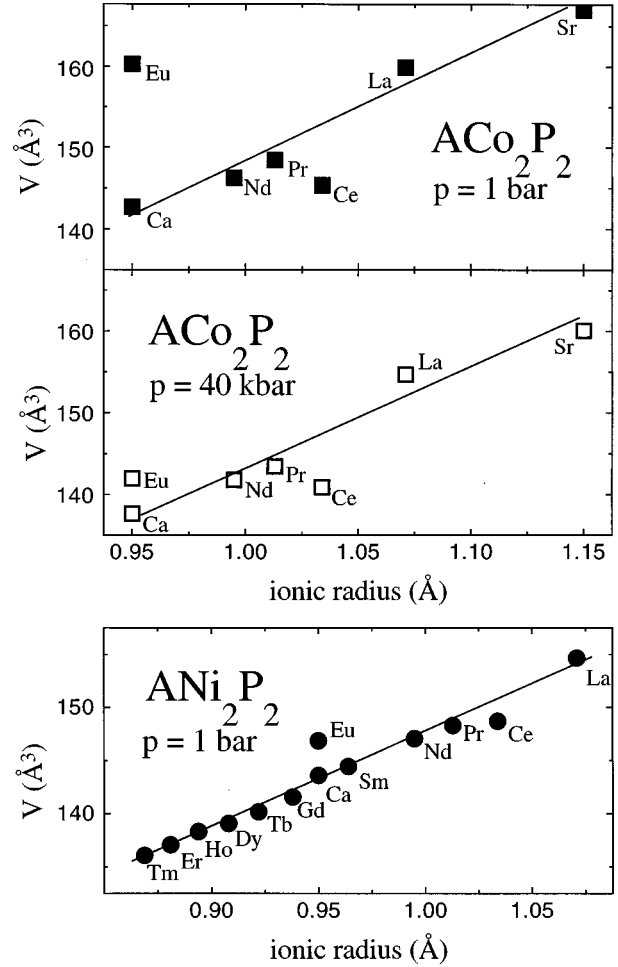


FIG. 6. Unit-cell volume at ambient pressure (top) and 40 kbar (middle) as function of the ionic radii of the A element (see text) in ACo_2P_2 and corresponding data for ANi_2P_2 at 1 bar (Ref. 1).

increasing pressure ($\Delta d_{Co-P} = +1.6\%$).

The compounds of ACo_2P_2 stoichiometry again can be divided into two groups: those with a long P-P distance ($d_{P-P} > 3 \text{ \AA}$) and long bond lengths from the A element to P or Co, but a rather short Co-P distance. $SrCo_2P_2$, $LaCo_2P_2$, and $EuCo_2P_2$ (low-pressure phase) belong to this group. The P-P distance of these compounds decreases strongly with increasing pressure [Fig. 10(a)] and it also decreases with increasing temperature [Fig. 10(b)].

TABLE III. Thermal expansion of the $ThCr_2Si_2$ type phosphides of ACo_2P_2 stoichiometry [$A = Sr, Pr, Nd, Eu$ (sample 1)]. The thermal expansions α_I ($I = a, c, V$) were obtained by a linear fit to the data between the given temperatures T_1 and T_2 by using $\alpha_I = [1/I(T_1)](\Delta I/\Delta T)$.

Compound	Temperature range	$\alpha_a (10^{-5}/K)$	$\alpha_c (10^{-5}/K)$	$\alpha_V (10^{-5}/K)$	α_c/α_a
$SrCo_2P_2$	300 – 680 K	2.22(3)	0.36(1)	4.84(6)	0.16
$EuCo_2P_2$	300 – 860 K	1.94(1)	0.02(3)	3.93(3)	0.01
$PrCo_2P_2$	400 – 600 K	-0.55(3)	9.79(8)	8.69(6)	-18
$NdCo_2P_2$	300 – 500 K	0.57(3)	3.94(2)	5.08(7)	7
$NdCo_2P_2$	650 – 850 K	0.63(3)	6.3(1)	7.5(1)	10

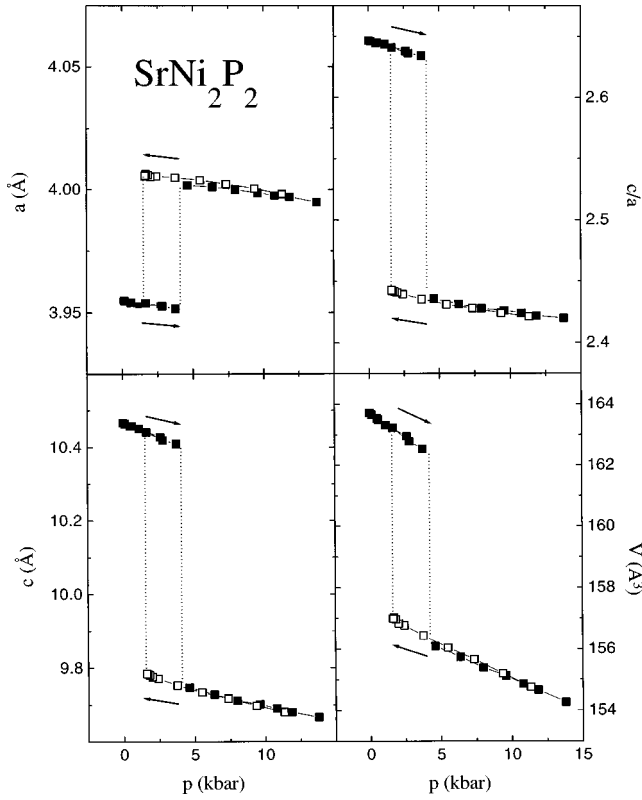


FIG. 7. Lattice parameter of SrNi_2P_2 as function of pressure.

On the other hand the ACo_2P_2 compounds containing Ca, Eu (high-pressure phase) or the smaller rare-earth elements Ce, Pr, or Nd are characterized by rather long Co-P bonds, short A-P and A-Co bonds, and a rather short P-P bond length. However, in PrCo_2P_2 $d_{\text{P-P}}$ increases strongly with increasing temperature to about 2.7 \AA at 750 K .

In a recent publication⁸ which deals with the corresponding ThCr_2Si_2 -type compounds of ARh_2P_2 stoichiometry the shorter P-P bonds are — according to band-structure calculations⁷ — caused by a P-P single bond perpendicular to the layers, while there is no P-P bond at all for the longer ones. The P-P distance of PrCo_2P_2 , which makes up about 2.7 \AA at 750 K , exceeds the usual one of a P-P single bond even at stp [$d_{\text{P-P}} = 2.569 \text{ \AA}$ (Ref. 10)] significantly, but was claimed to be not long enough to be classified as a nonbonding P-P state.^{10,6} It was supposed that the P-P atoms in the extended P-P bond should obtain an oxydation number of -2.5 , corresponding to the middle of -2 (P atoms in a P-P single bond) and -3 (isolated P atoms).

In the framework of self-consistent linear muffin-tin orbital band-structure calculations⁷ the behavior of the bond lengths as function of pressure of the measured compounds can be essentially explained by their electronic structure. This is done more extensively in order to explain the phase transition occurring in ARh_2P_2 ($A = \text{Eu}, \text{Sr}$).⁸ By filling the d shell the P-P bonding states become more populated. Hence, the compounds containing transition metals from more to the right of the periodic table tend to form stronger, i.e., shorter P-P bonds, which is most clearly visible by replacing Co in EuCo_2P_2 by Ni ($\Delta d_{\text{P-P}} \approx -28\%$). An increasing electron number in AT_2P_2 compounds populates also T -P antibonding states leading — consistent to the ex-

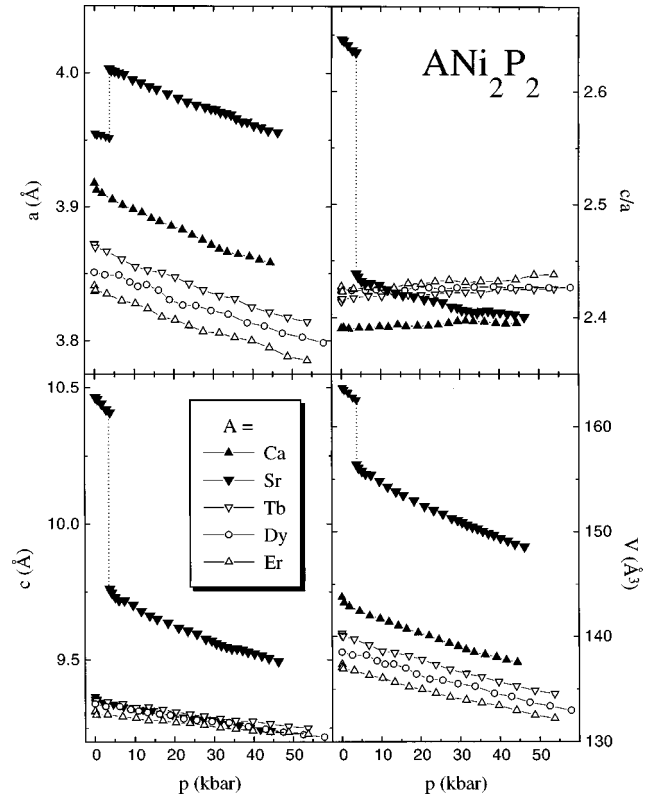


FIG. 8. Lattice parameter of ANi_2P_2 ($A = \text{Ca}, \text{Sr}, \text{Tb}, \text{Dy}, \text{Er}$) as function of pressure.

perimental results — to longer T -P bonds.⁸ If the T -P layers are separated, for instance, due to large A atoms like Ba, it is not possible to form a short P-P contact by geometric reasons. By approaching the phase transition in EuCo_2P_2 from the high-pressure phase a critical P-P distance is reached. The following sudden depopulation of P-P bonding and Co-P antibonding states leads to the extreme increase of the P-P distance and to stronger Co-P bonds, i.e., an increase of c whereas a decreases.

Parallel to this explanation of the phase transition by the electronic structure a consideration of strain effects occurring in the vicinity of the phase transition also makes the occurrence of a phase transition plausible:⁸ In the high-pressure phase of EuCo_2P_2 the Eu is confined by a cage of covalently bonded Co and P atoms (see Fig. 1). Due to the large Eu atom the Eu-P and Eu-Co bonds are in this phase compressed and, consequently, the P-P and Co-P bonds are

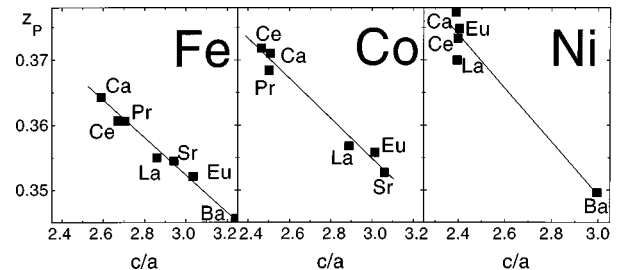


FIG. 9. Dimensionless parameter z_p as function of c/a for various AT_2P_2 compounds ($T = \text{Fe}, \text{Co}, \text{Ni}$).

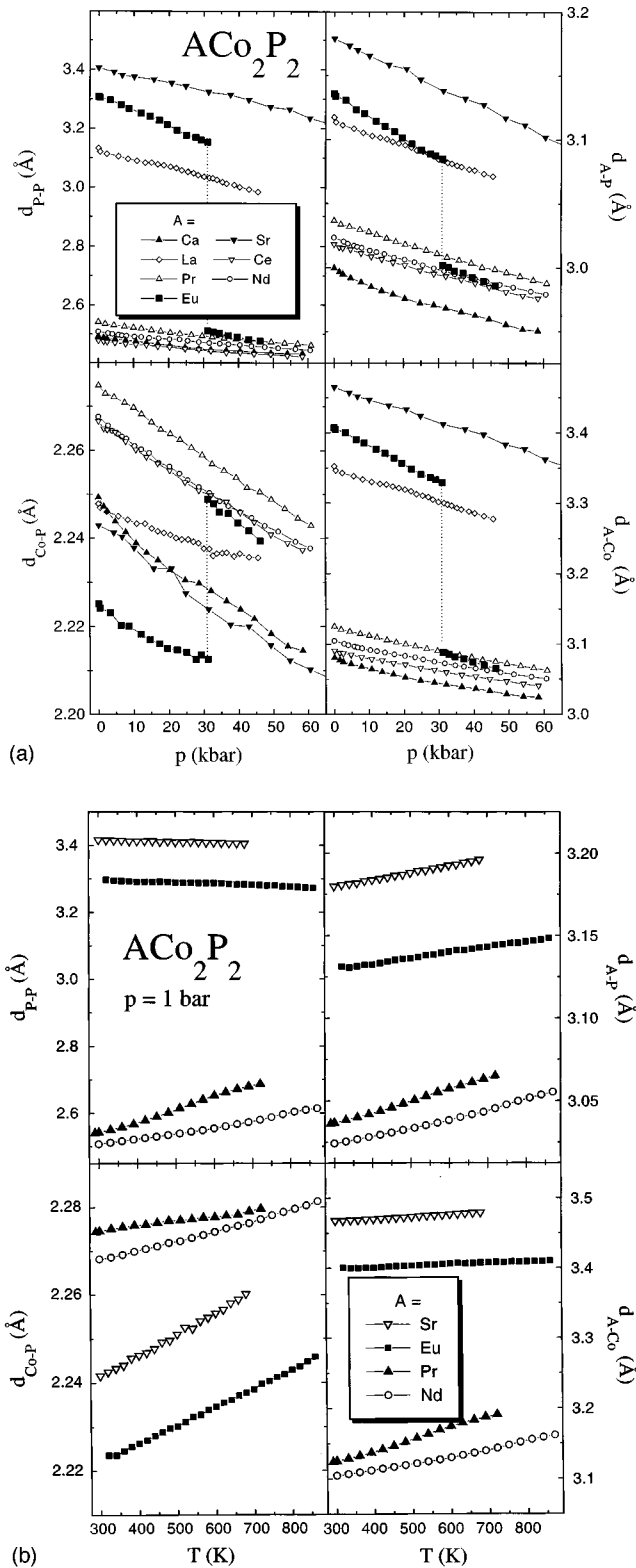


FIG. 10. Bond lengths in ACo_2P_2 calculated from the lattice constants as function of pressure (a) and of temperature (b) by assuming a linear dependence of z_p on c/a (see text).

expanded. With decreasing pressure at the phase transition the P-P bond length exceeds the critical distance which is necessary for a P-P single bond. Hence, an expansion of the Eu-P and Eu-Co bonds as well as a contraction of the Co-P bond is possible now. Together this leads to the extreme increase of d_{P-P} .

Similar to $EuCo_2P_2$ also in $SrNi_2P_2$ the pressure dependence of the lattice parameters, which change at the phase transition in the same anisotropic way, is strongly correlated with a change of the P-P distance. However, the reason for the strongly reduced change of the lattice parameters at the phase transition, which make up only about the half of those of $EuCo_2P_2$, is given by the above-mentioned superstructure observed in $SrNi_2P_2$ at stp.¹⁵ Essentially responsible for this superstructure is a displacement of the atoms from their ideal position, which is essentially due to two strongly different P-P distances along [001]: $d_{P_1-P_1} = 2.45$ Å and $d_{P_2-P_2} = 3.28$ Å.¹⁵ Referring to this, $SrNi_2P_2$ can be classified somehow between those compounds with a P-P single bond and those without it. Assuming an undistorted $ThCr_2Si_2$ structure type in the high-pressure phase of $SrNi_2P_2$ the P-P distance along the c direction can be — by using the linear correlation between c/a and z_p — roughly estimated to about 2.45 Å corresponding to an elongated P-P single bond. Actually, a further phase transition was found in $SrNi_2P_2$ as function of temperature (ambient pressure) at about 320 K.¹⁵ In the high-temperature phase ($T > 320$ K) $SrNi_2P_2$ crystallizes in the undistorted $ThCr_2Si_2$ structure type again with only one P-P distance ($d_{P-P} = 3.12$ Å) corresponding to a nonbonding P-P state.

A further observation is enhanced compressibilities by approaching the phase transitions in $SrNi_2P_2$ and $EuCo_2P_2$. They can be demonstrated by figuring the bulk modulus of the measured ANi_2P_2 compounds as function of their valence electron density q/V_0 (q : valence electron number of the A element, V_0 : volume of the unit cell at stp). In order to work at comparable data all bulk moduli B shown in Fig. 11 as function of q/V_0 are obtained by compressibility determination in the pressure range below 30 kbar ($SrNi_2P_2$: 5 kbar $< p < 30$ kbar). Except for $PrCo_2P_2$ we found a rather linear dependence (dotted line) of B on q/V_0 for all compounds that show no phase transition. A similar dependence was, for instance, also observed in RCu_2Si_2 (Ref. 16) and RB_6 .¹⁷

Bulk moduli, which are significantly smaller than expected by this linear correlation, were determined for $EuCo_2P_2$ (low-pressure phase), $SrNi_2P_2$ (high-pressure phase), and $PrCo_2P_2$.

The small bulk modulus of $PrCo_2P_2$ is mainly due to the enhanced compressibility of the c axis below 20 kbar whereas κ_a is slightly reduced (see Table II). The anisotropic behavior of the lattice constants of $PrCo_2P_2$ in this pressure range strongly reminds one of that of $SrNi_2P_2$ above 15 kbar (see Table II) and can be explained by the electronic band structure: coming from high pressures a depopulation of P-P bonding states and Co-P antibonding states is in our opinion responsible for the large ratio κ_c/κ_a in the vicinity of the phase transition.

This explanation for this anisotropic behavior of the lattice constants is quite similar to the one, which was used to explain the occurrence of the first-order phase transitions (see above). However, the changes of the electronic structure and of the lattice constants at the phase transitions are — contrary to those in the vicinity of the phase transitions — extremely strong. Hence, we regard the anisotropic changes of the lattice parameters of $SrNi_2P_2$ and also those of $PrCo_2P_2$ below 20 kbar as precursors of a phase transition. The same mechanism, i.e., a depopulation of P-P bonding

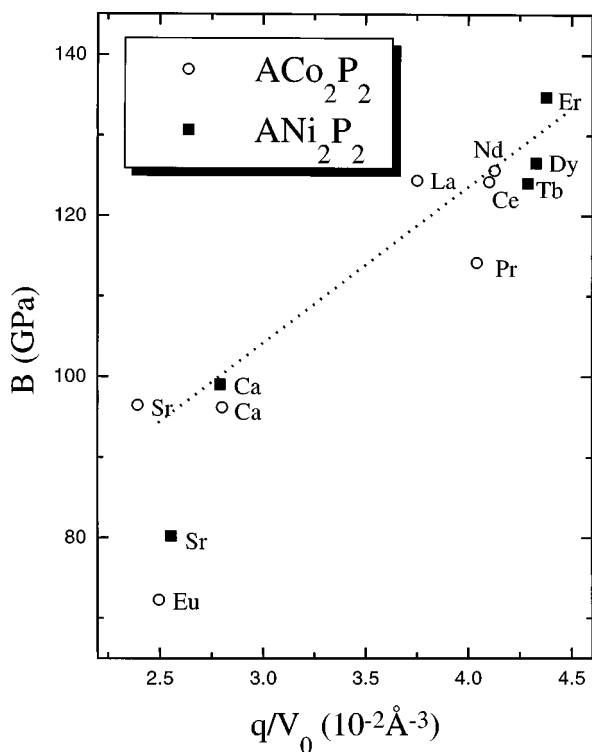


FIG. 11. Bulk modulus B of the measured AT_2P_2 compounds as function of the valence electron density q/V_0 (see text). The bulk moduli of the integral valent compounds exhibiting no phase transition depend rather linearly on q/V_0 (dotted line).

and Co-P antibonding states, is in our opinion responsible for the extreme increase of the c/a ratio in PrCo_2P_2 with increasing temperature (see Table III), too.

Because of the extremely strong changes of the lattice parameters at the phase transitions in SrNi_2P_2 and EuCo_2P_2 we cannot exclude that — on top of the above-mentioned electronic reasons — strain effects contribute in the vicinity of the phase transitions to the enhanced volume compressibility. In addition effects of a slight valence change of Eu may be also responsible for the large volume compressibility by approaching the phase transition in EuCo_2P_2 at 31 kbar.

VI. CONCLUSIONS

By performing x-ray-diffraction measurements as function of pressure ($T = 300$ K) in EuCo_2P_2 and SrNi_2P_2 a first-order phase transition with an enormous hysteresis and

extremely strong and anisotropic changes of the lattice parameters was observed at 30 kbar and 4 kbar, respectively. The phase transition is strongly correlated with a change of the P-P distance perpendicular to the layers. In the high-pressure phase of both compounds the P-P distance along the c axis can be estimated to be in the range of an elongated P-P single bond. While SrNi_2P_2 crystallizes at stp in a distorted ThCr_2Si_2 structure type¹⁵ — containing P-P distances in the range of a P-P single bond as well as those corresponding to no P-P bond — the compound EuCo_2P_2 crystallizes in the undistorted ThCr_2Si_2 type containing only one P-P distance which is larger than 3.1 Å (no P-P bond).

Concerning the dependence of the lattice parameters and bond lengths on pressure or temperature we can clearly distinguish two groups of ACo_2P_2 compounds: Those with no P-P bond, i.e., SrCo_2P_2 , LaCo_2P_2 , and EuCo_2P_2 (low-pressure phase) and those with a P-P single bond [ACo_2P_2 ($A = \text{Ca, Ce, Pr, Nd, and Eu}$, high-pressure phase)]. The extremely strong increase of $d_{\text{P-P}}$ in trivalent PrCo_2P_2 by increasing temperature may be interpreted as the beginning of a continuous phase transition towards a P-P state without a P-P bond. Measurements of the lattice parameters on LaCo_2P_2 as a function of pressure up to 250 kbar, which are planned in the near future, will probably clarify, whether a (continuous) phase transition also occurs in trivalent rare-earth compounds of ACo_2P_2 stoichiometry.

From the structural point of view the phase transition in EuCo_2P_2 is connected with a valence change: with increasing pressure it changes from Eu^{2+} towards trivalent or intermediate valent Eu. In order to study changes of the Eu valence and of the magnetism at the phase transition ¹⁵¹Eu Moessbauer measurements on EuCo_2P_2 as function of pressure and temperature are in progress.¹⁸ The magnetic structure of EuCo_2P_2 at ambient pressure was already studied in detail by neutron-diffraction experiments on a single crystal.¹⁹ Pressure-dependent neutron-diffraction experiments are planned.

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