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# Structural study of $U(Pd_{1-x}Fe_x)_2Ge_2$ at high pressure

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**Abstract**

The crystal structure of the $U(Pd_{1-x}Fe_x)_2Ge_2$ compounds with Fe content $x = 0$–$0.03$ and the crystal and magnetic structure of $U(Pd_{0.98}Fe_{0.02})_2Ge_2$ at high external pressures up to 4.5 GPa were studied by means of powder neutron diffraction in the temperature range 1.5–300 K. With increasing Fe content the values of the lattice parameters and interatomic distances change only slightly, but it is known from previous experiments that the magnetic structure changes drastically for $x \geqslant 0.015$. In contrast to this, high external pressure modifies the crystal structure more significantly while the magnetic structure remains unchanged. The results obtained allow one to infer that drastic changes in the magnetic structure of the $U(Pd_{1-x}Fe_x)_2Ge_2$ compounds with increasing Fe content are a consequence of modification of the RKKY-type (RKKY standing for Ruderman, Kittel, Kasuya and Yosida) indirect exchange interaction due to the variation of the number of conduction electrons per U atom rather than a result of lattice contraction.

## 1. Introduction

Recent studies of $U(Pd_{1-x}Fe_x)_2Ge_2$ [1] have shown that even a small level of substitution of Fe atoms for Pd atoms ($x \sim 0.02$) leads to a drastic change in the magnetic properties of these compounds, while the type of the crystal structure remains unchanged ($ThCr_2Si_2$-type

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body-centred tetragonal structure; space group $I4/mmm$) [2, 3]. Pure $UPd_2Ge_2$ below the Néel temperature $T_N = 140$ K transforms from a paramagnetic to an antiferromagnetic (AF) state with incommensurate longitudinal spin-density-wave (LSDW) structure [4]. Another commensurate LSDW structure with 'squared' modulation and propagation vector $\boldsymbol{k} = (0, 0, 3/4)$ was observed in the temperature range 1.4–50 K. In the temperature range $50\ \mathrm{K} \leqslant T \leqslant 95$ K the magnetic structure is a mixture of these two phases and it gradually transforms from 'squared' to pure sinusoidal modulation with increasing temperature.

While $U(Pd_{0.99}Fe_{0.01})_2Ge_2$ shows similar behaviour, the low-temperature magnetic structure of $U(Pd_{0.98}Fe_{0.02})_2Ge_2$ becomes completely different [4, 5]. At $65\ \mathrm{K} < T < T_N = 135$ K, $U(Pd_{0.98}Fe_{0.02})_2Ge_2$ also exhibits incommensurate LSDW structure with sinusoidal modulation, but at $T < 65$ K the magnetic structure becomes a simple AF one with $\boldsymbol{k} = (0, 0, 1)$. In a very narrow temperature interval near 65 K, the AF and LSDW phases coexist. The sample with intermediate Fe concentration $U(Pd_{0.985}Fe_{0.015})_2Ge_2$ shows nearly the same behaviour as $U(Pd_{0.98}Fe_{0.02})_2Ge_2$ [18].

Thus, the magnetic structure of the $U(Pd_{1-x}Fe_x)_2Ge_2$ series undergoes significant changes with variation of the Fe doping level between $x = 0.01$ and 0.015. There have been several theoretical attempts to explain the magnetic phase diagram of the $A(M_{1-x}M'_x)_2Ge_2$ compounds. In [6], a phenomenological theory of magnetic phase transitions in such compounds, considering heterogeneities of the structure due to the presence of the doping element, was developed. It explains the change in the magnetic structure by a decrease in the unit-cell volume due to the substitution of Fe atoms for Pd ones.

In the $A(M_{1-x}M'_x)_2Ge_2$ compounds (except for $M/M' = Mn$) the magnetic moments are found only on the U atoms and are absent in transition metals. Since the distance between the nearest U atoms in these compounds is $d_{U-U} > 5$ Å, the direct exchange interaction is obviously negligible and the magnetic ordering of U magnetic moments should be related to an indirect exchange interaction [1, 7].

Endstra *et al* [8] constructed the phenomenological 'f–d hybridization model', which considers the ordering of 5f spins of U in the $U(M_{1-x}M'_x)_2Y_2$ compounds as a result of competition between the indirect f–d–f magnetic interaction of the local U magnetic moments (RKKY-type interaction, where RKKY stands for Ruderman, Kittel, Kasuya and Yosida) mediated by conduction electrons and the Kondo-type spin-compensating mechanism. This interaction is related to the conduction electron—f electron hybridization, whose strength may be characterized by the hybridization matrix element $V_{df}$. The calculated values of $V_{df}$ which depend on the U–M interatomic distance $d_{U-M}$ and the number of conduction electrons per U atom were used to explain the general experimentally observed features of the magnetic ordering of the $U(M_{1-x}M'_x)_2X_2$ compounds.

In [7], the magnetic phase diagram of the $U(M_{1-x}M'_x)_2X_2$ compounds was constructed using an isotropic one-dimensional indirect exchange model of RKKY type. It was shown that the magnetic ordering in these systems depends strongly on the number of conduction electrons per U atom.

The validity of these models can be checked by neutron diffraction experiments at high pressure. Application of high pressures will modify the strength of the d–f hybridization via a change of the U–M distance at fixed number of conduction electrons per U atom. In contrast to this, the effect of the variation of the Fe content $x$ ('chemical' pressure) modifies both interatomic distances and the number of conduction electrons per U atom. Hence, the comparison of external and 'chemical' pressure effects on the crystal and magnetic structure of the $U(Pd_{1-x}Fe_x)_2Ge_2$ compounds will allow one to clarify the role of the lattice contraction and the variation of the number of conduction electrons per U atom in the establishing of the magnetic ordering.

**Table 1.** Lattice parameters and unit-cell volume for U(Pd$_{1-x}$Fe$_x$)$_2$Ge$_2$ compounds at $T = 10$ K and ambient pressure with different Fe contents $x$.

| | $x = 0$ | $x = 0.02$ | $x = 0.03$ |
|---|---|---|---|
| $a$ (Å) | 4.181 86(2) | 4.177 21(3) | 4.175 96(3) |
| $c$ (Å) | 10.208 8(1) | 10.2090(1) | 10.2035(1) |
| $V$ (Å$^3$) | 178.531 | 178.130 | 177.936 |

## 2. Experimental details

Samples of U(Pd$_{1-x}$Fe$_x$)$_2$Ge$_2$ with $x = 0$–0.03 were studied. The details of the sample preparation are described in [9]. Neutron powder diffraction experiments with U(Pd$_{0.985}$Fe$_{0.015}$)$_2$Ge$_2$ were performed at the DMC diffractometer [10] (spallation source SINQ, PSI, Switzerland; incident wavelength $\lambda = 2.59$ Å) at high pressures up to 1.43 GPa and at the G6.1 diffractometer [11] (Orphée reactor, LLB, France; incident wavelength $\lambda = 4.75$ Å) at high pressures up to 4.4 GPa in the temperature range 1.5–300 K. Neutron powder diffraction experiments with U(Pd$_{0.98}$Fe$_{0.02}$)$_2$Ge$_2$ at high pressures up to 4.1 GPa in the temperature range 16–300 K were performed at the DN-12 TOF diffractometer [12] (IBR-2 pulsed reactor, FLNP JINR, Russia). The experiments at the DMC diffractometer were performed with the clamp high-pressure cell P15. The sample was mixed with NaCl and the known equation for the state of NaCl was used to determine the pressure on the sample. In the experiments with the G6.1 and DN-12 diffractometers, sapphire anvil high-pressure cells [13] were used. The pressure on the sample was determined by the ruby fluorescence technique.

To analyse the effect of chemical pressure on the crystal structure of the U(Pd$_{1-x}$Fe$_x$)$_2$Ge$_2$ compound with $x = 0$, 0.02 and 0.03 at ambient pressure in the temperature range 10–300 K, neutron powder diffraction experiments at the high-resolution Fourier RTOF diffractometer HRFD [14] (IBR-2 pulsed reactor, FLNP JINR, Russia) were also performed.

## 3. Results and discussion

The lattice parameters of the U(Pd$_{1-x}$Fe$_x$)$_2$Ge$_2$ compound ($x = 0$–0.03) obtained at ambient pressure and $T = 10$ K from the Rietveld refinement of the neutron diffraction data measured with the high-resolution ($\Delta d/d \sim 10^{-3}$) Fourier RTOF (reverse time-of-flight) diffractometer HRFD are presented in table 1. The Rietveld analysis was performed with the MRIA program [15] ($\chi^2 \sim 2.34$, $R_N = 9.8\%$). A structural model of the $I4/mmm$ space group with U atoms located at sites 2(a) (0, 0, 0), Pd/Fe atoms at sites 4(c) (1/2, 1/4, 0) and Ge atoms at sites 4(e) (0, 0, $z$) was used.

In previous experiments at ambient pressure with the pure UPd$_2$Ge$_2$ compound having the 'square' modulated LSDW structure, the appearance of first- and third-order satellites, which correspond to the first- and third-order harmonics of the magnetic moment, was observed at a low temperature [4]. In contrast to this, the doped U(Pd$_{0.985}$Fe$_{0.015}$)$_2$Ge$_2$ sample at low temperature and ambient pressure has a simple AF structure. In this case, only the first-order magnetic peaks with $h + k + l \neq 2n$ were observed [1]. Hence, the presence or absence of the third-order satellites at low temperature in the high-pressure diffraction patterns will indicate possible changes in the magnetic structure.

Figure 1 presents parts of the neutron diffraction patterns of U(Pd$_{0.985}$Fe$_{0.015}$)$_2$Ge$_2$ measured at $T = 1.5$ K, ambient pressure and high pressures of 0.4 GPa (DMC diffractometer) and 3.5 GPa (G6.1 diffractometer) in the regions of the (101) nuclear peak and the (101)$^-$

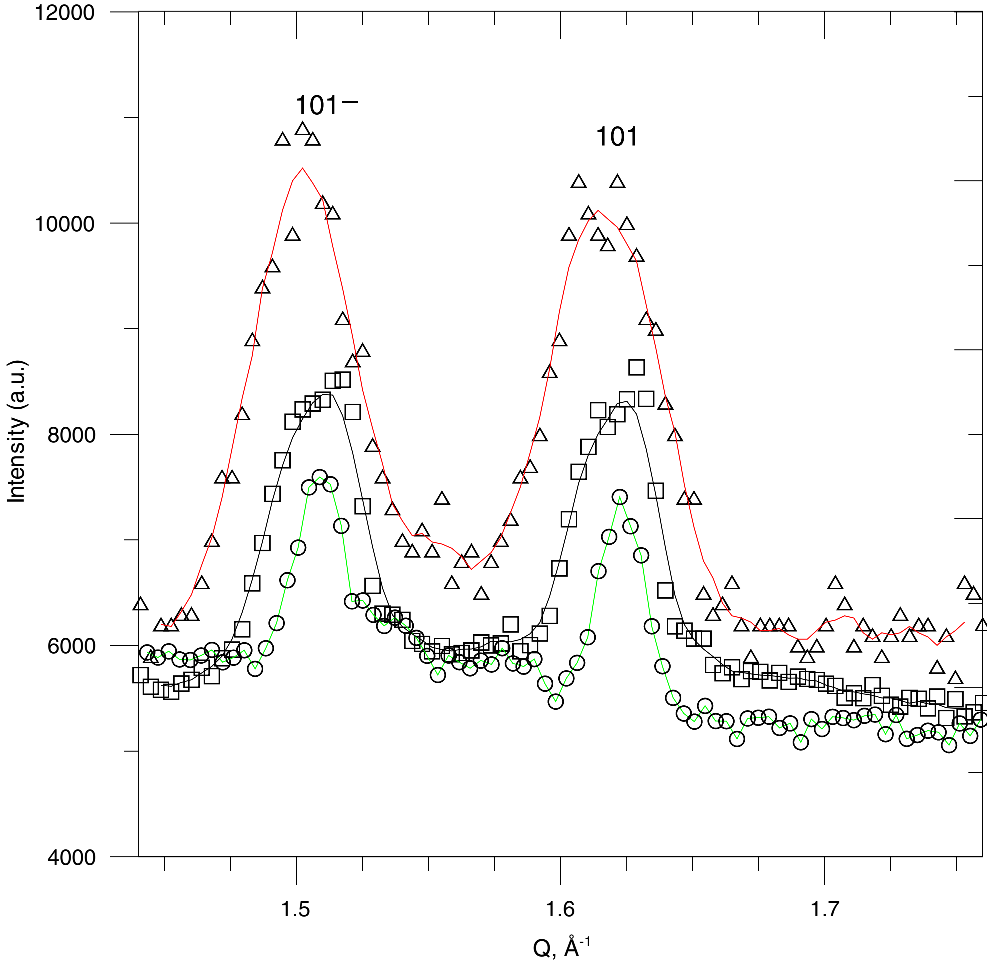

**Figure 1.** Parts of the neutron diffraction patterns of $U(Pd_{0.985}Fe_{0.015})_2Ge_2$ measured at $T$ = 1.5 K, ambient pressure and high pressures 0.4 GPa (DMC diffractometer) and 3.5 GPa (G6.1 diffractometer) in the regions of the (101) nuclear peak and the $(101)^-$ magnetic satellite peak. □: no pressure; ○: $P = 0.4$ GPa; △: $P = 3.5$ GPa.

(This figure is in colour only in the electronic version)

magnetic satellite peak. No third-order satellite between the (101) and $(101)^-$ peaks was found and no changes in the type of magnetic ordering under high pressure were observed within the experimental accuracy. The pressure-induced variation of the Néel temperature $T_N$ does not exceed 10 K.

Neutron diffraction patterns of $U(Pd_{0.98}Fe_{0.02})_2Ge_2$ measured at the DN-12 TOF diffractometer at pressures 0 and 4.1 GPa and ambient temperature are given in figure 2. Upon Rietveld refinement of the experimental data using the MRIA program, lattice parameters (figure 3) and interatomic distances (figure 4) of $U(Pd_{0.98}Fe_{0.02})_2Ge_2$ as functions of pressure were obtained. The calculated values of the linear compressibilities $k_a = -(1/a_0)(\mathrm{d}a/\mathrm{d}P)$ and $k_c = -(1/c_0)(\mathrm{d}c/\mathrm{d}P)$ are $k_a = 3.61 \times 10^{-3}$ GPa$^{-1}$ and $k_c = 0.79 \times 10^{-3}$ GPa$^{-1}$, respectively. They indicate the noticeable compression anisotropy of the lattice of $U(Pd_{0.98}Fe_{0.02})_2Ge_2$

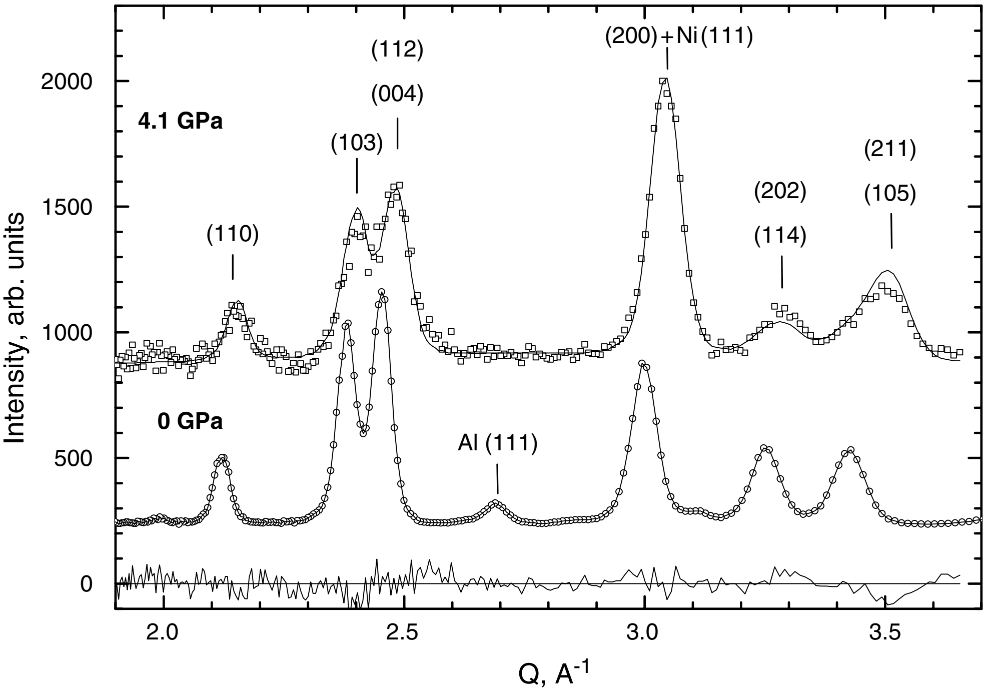

**Figure 2.** Neutron diffraction patterns of U(Pd$_{0.98}$Fe$_{0.02}$)$_2$Ge$_2$ measured at the DN-12 TOF diffractometer at pressures of 0 and 4.1 GPa and ambient temperature and processed by the Rietveld method. Experimental points, the calculated profile and the difference curve (for $P = 4.1$ GPa) are shown. Miller indices of the most intense diffraction peaks arising from the sample, the Al container used in the ambient pressure experiment and the Ni gasket of the high-pressure cell are shown.

with $k_a/k_c = 4.57$. The corresponding volume compressibility $k_V = -(1/V_0)(\mathrm{d}V/\mathrm{d}P)$ is $k_V = 7.97 \times 10^{-3}$ GPa$^{-1}$.

The comparison between the values obtained for the lattice parameters and interatomic distances (table 1, figures 3 and 4) shows that high external pressure induces more pronounced changes in the crystal structure of the U(Pd$_{1-x}$Fe$_x$)$_2$Ge$_2$ compound than the 'chemical' pressure (variation of the Fe content). An increase in the Fe content $x$ from 0 to 0.03 at fixed temperature $T = 10$ K leads to relative decreases in the lattice parameters, $\Delta a/a_0 = 1.41 \times 10^{-3}$, $\Delta c/c_0 = 5.19 \times 10^{-4}$, and interatomic distance U–M (M = Pd/Fe), $\Delta d_{\mathrm{U-M}}/d_{(\mathrm{U-M})0} = 8.49 \times 10^{-4}$. An increase in pressure up to 4.1 GPa leads to much larger changes of the corresponding values for U(Pd$_{0.98}$Fe$_{0.02}$)$_2$Ge$_2$: $\Delta a/a_0 = 1.48 \times 10^{-2}$, $\Delta c/c_0 = 3.24 \times 10^{-3}$ and $\Delta d_{\mathrm{U-M}}/d_{(\mathrm{U-M})0} = 7.89 \times 10^{-3}$ at ambient temperature. The $c/a$ ratio remains nearly the same with increase in $x$ at ambient pressure: $c/a \approx 2.44$ and increases slightly with increasing pressure up to 4.1 GPa from 2.44 to 2.46 (for the sample with $x = 0.02$). Certainly, such noticeable structural changes cannot be explained by the temperature difference of the lattice parameters and $d_{\mathrm{U-M}}$-values of the U(Pd$_{1-x}$Fe$_x$)$_2$Ge$_2$ compounds at $T = 10$ K and ambient temperature, which are nearly within the experimental accuracy (see figures 3 and 4 for $x = 0.02$).

In terms of the 'f–d hybridization model' [8], magnetic ordering features in the U(M$_{1-x}$M$'_x$)$_2$Y$_2$ compounds are related to the f–d hybridization strength, which is characterized by the values of the general hybridization matrix elements $V_{\mathrm{df}}$. These values

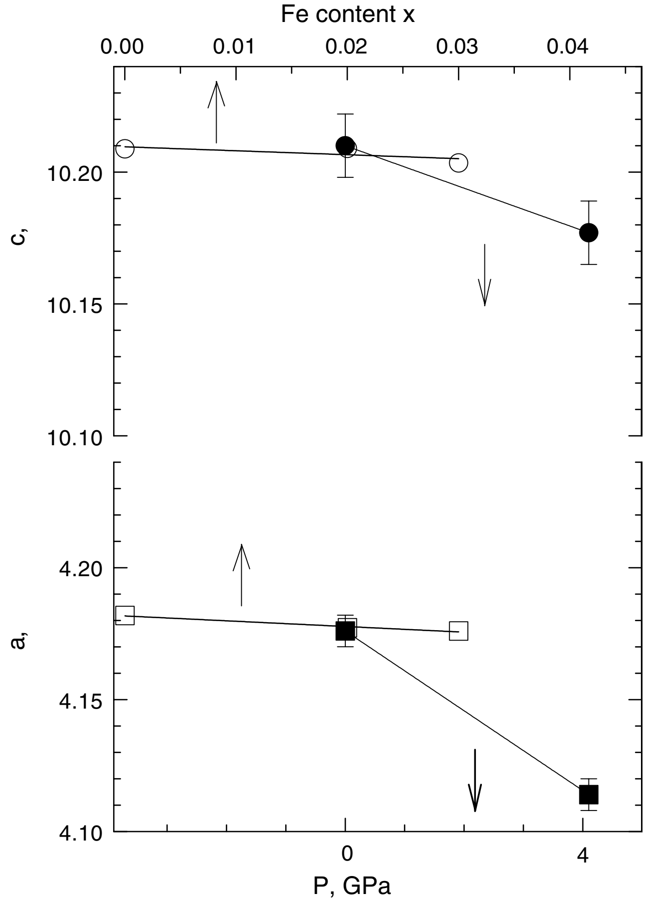

**Figure 3.** Open symbols: lattice parameters of $U(Pd_{1-x}Fe_x)_2Ge_2$ compounds as functions of Fe content $x$ at $T = 10$ K. Solid lines represent linear fits to the experimental data. The error bars are within the symbol size. Black symbols: lattice parameters of $U(Pd_{0.98}Fe_{0.02})_2Ge_2$ as functions of pressure at ambient temperature. Solid lines represent the high-pressure behaviour of the lattice parameters expected in the linear approach.

are proportional to the $d_{\mathrm{U-M}}$-distance as $V_{\mathrm{df}} \propto 1/d^6_{\mathrm{U-M}}$ and hence one would expect an external high pressure to induce more pronounced changes in the magnetic structure of $U(Pd_{1-x}Fe_x)_2Ge_2$ than the variation of the Fe content. However, this assumption is not supported by the experimental data.

In the isotropic one-dimensional RKKY-type model [7], the main factor which most strongly affects the magnetic ordering of $U(M_{1-x}M'_x)_2Y_2$, is the number of conduction electrons per U atom. The application of high external pressure could not change this number significantly. To analyse the effect of Fe substitution on its value at ambient pressure, we may estimate the number of conduction electrons per formula unit using the free-electron gas model [16, 17] as

$$Z = 0.006A/\rho(k_p)^{3/5}.$$

Here $A$ is the molar weight of material (in g mol$^{-1}$), $\rho$ is the mass density of the material (in g cm$^{-3}$) and $k_p$ is the isotropic linear compressibility. As a first approximation, we may neglect

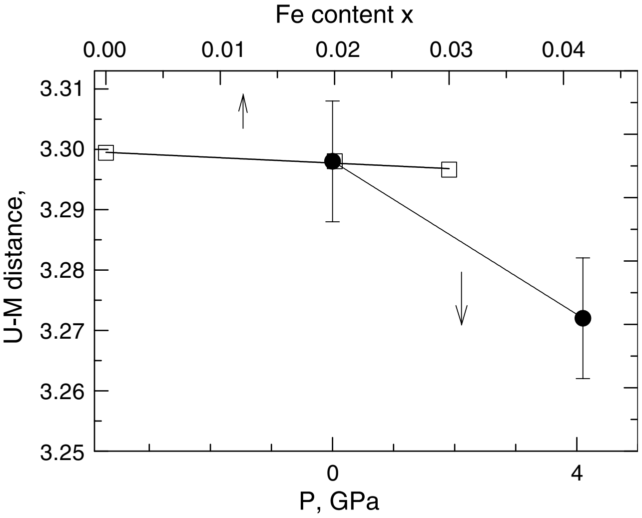

**Figure 4.** Open symbols: the interatomic distance U–M (M = Pd/Fe) in U(Pd$_{1-x}$Fe$_x$)$_2$Ge$_2$ compounds as a function of Fe content $x$ at $T = 10$ K. The solid line represents a linear fit to the experimental data. The error bars are within the symbol size. Black symbols: the interatomic distance U–M in U(Pd$_{0.98}$Fe$_{0.02}$)$_2$Ge$_2$ as a function of pressure at ambient temperature. The solid line represents the high-pressure behaviour of the U–M distance expected in the linear approach.

the difference in linear compressibility of U(Pd$_{1-x}$Fe$_x$)$_2$Ge$_2$ for small Fe content $x \leqslant 0.03$ and use for estimates of the linear compressibility averaged between $(k_a, k_c)$ values the value $k_p = 2.67 \times 10^{-3}$ GPa$^{-1}$. The calculated number of conduction electrons per U atom increases from $Z = 11.07$ to 11.27 with increase of the Fe content $x$ from 0 to 0.03. The calculations performed for the similar compound UNi$_2$Ge$_2$ [7] showed that comparable variation of $Z$ in the interval 11–12 results in drastic changes of the magnetic ordering.

## 4. Conclusions

In this work we have analysed the effects of Fe substitution and external high pressure on the crystal and magnetic structure of U(Pd$_{1-x}$Fe$_x$)$_2$Ge$_2$ with $x = 0$–0.03. The Fe substitution modifies the crystal structure of these compounds only slightly and leads to drastic changes in the magnetic structure. In contrast to this, the application of high external pressure results in more noticeable changes of lattice parameters and interatomic distances while the magnetic structure does not change.

The observed changes of the magnetic structure of U(Pd$_{1-x}$Fe$_x$)Ge$_2$ caused by Fe substitution of Pd atoms at ambient pressure could not be explained in terms of the ‘f–d hybridization model’ by the modification of hybridization matrix elements, since their values $V_{\mathrm{df}} \propto 1/d^6_{\mathrm{U-M}}$ and the U–M distance vary only very slightly for the Fe doping level studied, $x < 0.03$.

A possible explanation of the drastic changes in the magnetic structure of U(Pd$_{1-x}$Fe$_x$)$_2$Ge$_2$ caused by Fe substitution is the modification of the RKKY-type indirect exchange interaction via variations of the number of conduction electrons per U atom.

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