The coexistence of two phases with ordered and disordered vacancies in $PrGe_{1.6}$

B Lambert-Andron†, J Pierre‡, B Chenevier§, R Madar§, N Boutarek§ and J Rodriguez-Carvajal‖

† Laboratoire de Cristallographie, CNRS, 166 X, 38042 Grenoble, France
‡ Laboratoire L Néel, CNRS, 166 X, 38042 Grenoble, France
§ Institut National Polytechnique de Grenoble, ENSPG, BP 46, 38042 St Martin d'Hères, France
‖ Laboratoire L Brillouin, CEN Saclay, 91191 Gif sur Yvette, France

Abstract. The $PrGe_{1.6}$ compound shows two coexistent crystallographic structures, which are ordered and disordered variants of the $ThSi_2$ structure, the ordered phase resulting from the ordering of Ge vacancies. Comparison is made with $CeGe_{1.6}$ and Ce and Pr silicides, which exhibit the same type of phase separation.

1. Introduction

Numerous long-range phase separations have been observed in metallic compounds, such as precipitation phenomena, spinodal decomposition and eutectic or eutectoid (peritectic or peritectoid) reactions. The important parameters in order to establish the basis for the understanding of this phenomenon are the atomic composition and crystallographic structure of each phase, their volume fraction and the size and shape of each domain. Different experimental techniques must be used in order to determine these features, and to try to understand the fundamental mechanisms involved in the transformation.

The driving mechanisms for these solid state transformations can be of different natures: structural instabilities, long-range ordering of atoms leading to superstructures, etc. Special mention can be made of non-stoichiometric compounds, and particularly those involving vacancies.

Among binary compounds, rare earth silicides and germanides RSi_{2-x} and RGe_{2-x} show a systematic occurrence of vacancies, and a large variety of crystallographic structures, which depend on the rare earth element, the stoichiometry and the temperature.

The ordering of vacancies as a function of temperature induces phase separations linked to the coexistence of ordered and disordered phases: such phenomena have been already observed for instance in $CeSi_{2-x}$ [1], $PrSi_{2-x}$, $CeGe_{2-x}$ [3] and $PrGe_{2-x}$ [4]. These phenomena were revealed through x-ray and neutron diffraction, magnetization and electrical transport studies. Electron microscopy [1] has shown the existence of superstructures at low temperature in some cases where x-ray and neutron diffraction failed to reveal them.

Schobinger-Papamantellos *et al* [5] performed a crystallographic study of $PrGe_{2-x}$ compounds for $0.1 < x < 0.5$; they observed only one phase, with a rapid variation of lattice parameters around $PrGe_{1.7}$ (table 1). Conversely, recent work [4] on the $PrGe_{2-x}$ system has shown the coexistence of two closely related phases for $x = 0.6$ at room

Table 1. The variation of lattice parameters as a function of Ge content (after Schobinger-Papamantellos *et al* [5] (s)), and those of ordered and disordered $PrGe_{1.6}$ phases (room temperature data). Lattice parameters are given for the basic cell $ThSi_2$.

Composition	a (Å)	c (Å)
$PrGe_{1.55}$ (s)	4.196	14.145
$PrGe_{1.6}$ (s)	4.193	14.152
$PrGe_{1.6}$ (ordered)	4.192(3)	14.07(1)
$PrGe_{1.6}$ (disordered)	4.228(4)	14.00(1)
$PrGe_{1.75}$ (s)	4.254	13.986
$PrGe_{1.80}$ (s)	4.261	13.973

temperature and below. In the following, we describe the results of high-resolution neutron and x-ray powder diffraction studies on the $PrGe_{1.6}$ compound. One notes that it is difficult to obtain large single crystals when such phase transformations are involved, even if mixed phase crystals can be obtained for microscopy investigations or magnetic measurements [3]. Moreover, studies of crystals containing two phases in a more or less exact epitaxial relation are not so simple.

2. A summary of previous studies

Light rare earth silicides or germanides generally crystallize with a tetragonal $ThSi_2$ structure (space group $I4_1/amd$), or superstructures related to the ordering of vacancies. For Ce and Pr silicides, a phase separation has been observed at about 200 K, leading at lower temperature to the coexistence of two phases [1,2]. For $CeGe_{2-x}$ ($0.3 < x < 0.4$) or $PrGe_{1.6}$ (bulk stoichiometry), it has been observed that two different phases coexist at room temperature, one being a disordered $ThSi_2$ phase, the other a superstructure $(3a, 3a, c)$ of $ThSi_2$. The structures of the two phases of $CeGe_{1.6}$ have been refined by Lambert-Andron *et al* [6]. The ordered phase has a smaller a parameter and a larger c parameter than the disordered phase, the volume being smaller by 1.4%. This is related to a preferential ordering of vacancies, with a succession of dense and vacant planes of Ge along the c axis. After structural refinement, the compositions of the two phases were found to be so close that they could not be separated from the average, within experimental uncertainty.

3. Neutron and x-ray high-resolution studies

A bulk sample of nominal composition $PrGe_{1.6}$ was melted using the cold crucible induction technique described earlier [7], and annealed for 4 d at 850 °C. It was ground to powder just before neutron study.

Neutron powder diffraction was performed at the Leon Brillouin Laboratory (LLB) in Saclay, using diffractometer D1A. This high-resolution diffractometer comes from the Institut Laue–Langevin (ILL), and was installed at LLB during the refurbishment of the ILL reactor. The incident wavelength was 2.58 Å for low-temperature studies (1.5, 16, 25 K). A subsequent experiment at room temperature was performed at 1.98 Å wavelength.

At 300 and 25 K, the diffraction patterns (figure 1) can be explained by considering nuclear scattering from two phases, the main phase (Q1) being a superstructure of $ThSi_2$,
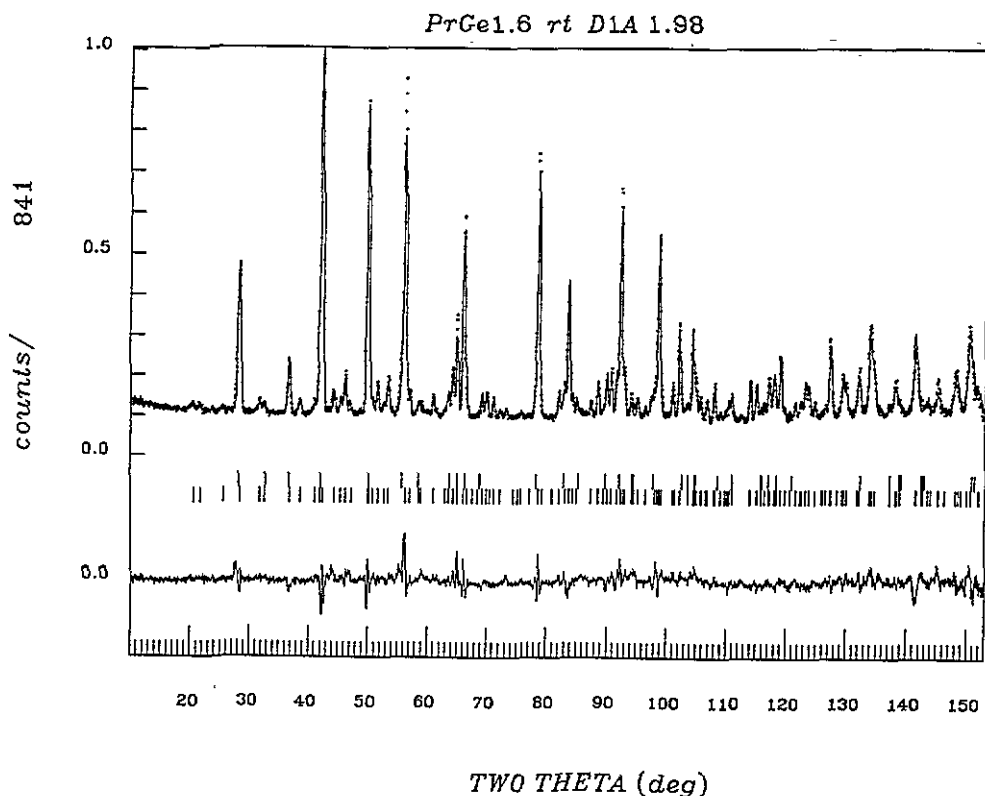
Figure 1. The neutron diffraction pattern for PrGe$_{1.6}$ at room temperature, and the Rietveld fit.

the minor phase (Q2) having the ThSi$_2$ structure with disordered vacancies (figure 2). The lattice parameters at room temperature are given in table 1.

All the weak lines of the superstructure QI can be indexed either with an orthorhombic cell ($a = \sqrt{2}a_t$, $b = 3\sqrt{2}a_t$, c) as observed for Tb$_3$Ge$_5$ (space group $Fdd2$) [5], or with a tetragonal cell ($a = 3a_t$, c), space group $I4_1$, like CeGe$_{1.6}$ [6]. The symmetry cannot be ascertained without a single-crystal study. The structure refinement was started assuming the $Fdd2$ space group, using the Rietveld program FULLPROF [8]. The refined atomic positions and thermal parameters at room temperature are given in table 2 for the two phases. The proportion of each is 18% for the disordered phase and 82% for the ordered one, the refined composition being the same: PrGe$_{1.60(5)}$ for the two phases within experimental uncertainty. The reliability factors are $R_p = 6\%$, $R_{wp} = 7\%$, $R_{exp} = 3\%$, where the profile reliability factor is

$$R_p = \sum |Y_o - Y_c| \Big/ \sum |Y_o|$$

the weighted reliability factor

$$R_{wp} = \left[\sum w|Y_o - Y_c|^2 \Big/ \sum w|Y_o|^2 \right]^{1/2}$$

and the expected reliability factor

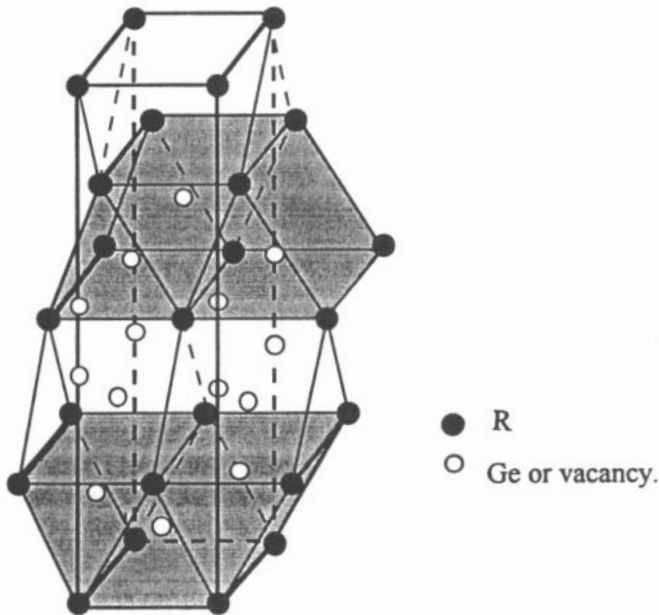$$R_{exp} = \left[F \Big/ \sum wY_o^2 \right]^{1/2}$$

Figure 2. The structure type ThSi$_2$ ($I4_1/amd$). For the disordered phase, vacancies are distributed randomly on Ge sites, whereas more or less dense Ge planes occur successively along the c axis in the ordered phase. A more complete figure concerning the $Fdd2$ ordered structure can be found in [9].

Table 2. Structural parameters of PrGe$_{1.6}$ with ordered vacancies (Q1) and disordered vacancies (Q2).

Atom	Site	x	y	z	B (Å^2)	p
Q1						
Pr1	8a	0	0	0	0.70(5)	0.5
Pr2	16b	0.758(1)	0.0796(5)	0.259(1)	0.70(5)	1
Ge1	8a	0	0	0.441(1)	0.28(15)	0.44(1)
Ge2	16b	0.791(1)	0.0716(5)	0.658(1)	1.20(1)	0.94(1)
Ge3	16b	0.739(1)	0.0860(5)	0.837(1)	1.20(1)	1.00(1)
Ge4	8a	0	0	0.615(1)	0.28(15)	0.07(1)
Q2						
Pr	4a	0	0	0	0.4(2)	0.125
Ge	8e	0	0	0.580(2)	2.3(3)	0.20(1)

Y_o and Y_c are the observed and calculated intensities and F the number of degrees of freedom.

The refinement starting with the $I4_1$ structure for Q1 gives atomic positions close to those found for CeGe$_{1.6}$ [6], with $R_p = 7\%$, $R_{wp} = 9\%$, $R_{exp} = 3\%$.

It is difficult in this case to obtain convervence for structures having pseudosymmetry like Q1 because of high correlations between parameters; constraints between the isotropic thermal parameters were needed to obtain stable refinement.

X-ray diffraction studies were performed at room temperature using a Siemens high-resolution D500 diffractometer (figure 3). The powder previously examined by neutron
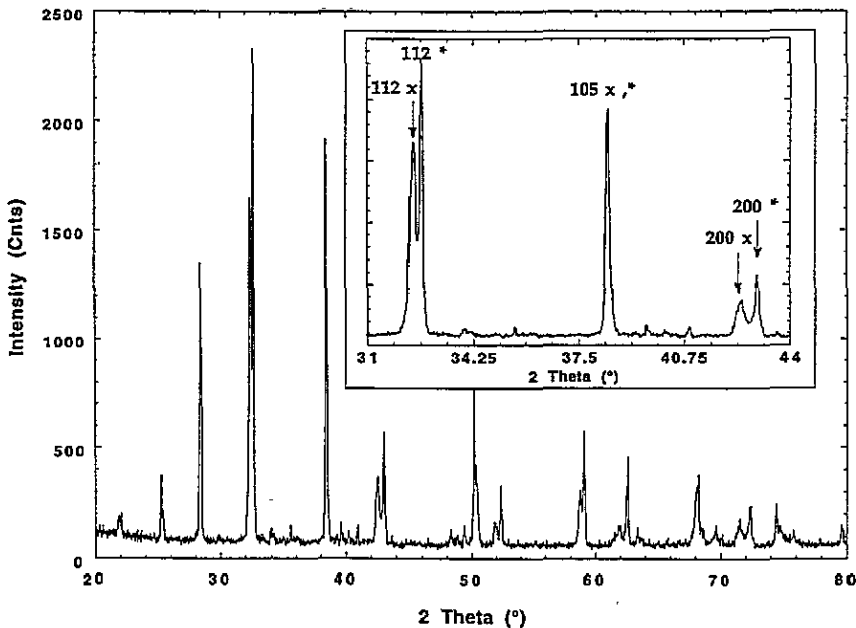
Figure 3. The x-ray diffraction pattern at room temperature. The inset enlarges a part of the pattern; Bragg reflections from the ordered phase are labelled by $*$, those for the disordered phase by $\times$.

diffraction was crushed to a finer grain size, in order to obtain better statistics on line intensities.

An important feature of x-ray high-resolution patterns (not clearly seen in neutron data) is a clear separation of Bragg reflections from each phase (the inset of figure 3), and a large difference between the widths of these reflections for the ordered and disordered phases, both being wider than the experimental resolution (figure 4). The width for the disordered phase is about twice that of the ordered phase.

Finally, we observed an increase in the proportion of the disordered phase between neutron experiments and subsequent x-ray characterization, which could be the result of ageing or milling of the powder.

4. Magnetic structures

From the analysis of the difference pattern between $T = 1.5$ K and 25 K, both phases are found to be ferromagnetic at 1.5 K, in agreement with magnetic measurements on a single crystal [4]. During resistivity measurements, two kinks in the resistivity have been observed at 19 and 14 K. By analogy with CeGe$_{1.6}$, where the two crystallographic structures order at different temperatures (with different types of magnetic order), we may suppose that the two phases of PrGe$_{1.6}$ order ferromagnetically with different Curie points. In principle, the neutron pattern taken at 16 K should give some information about that point; however the statistics and resolution of the neutron pattern are not good enough to distinguish which phase has the higher Curie point.

The refinement of the magnetic structure was done using the program MXD [10], assuming the same magnetic moment in the two phases, and noting that the atomic positions
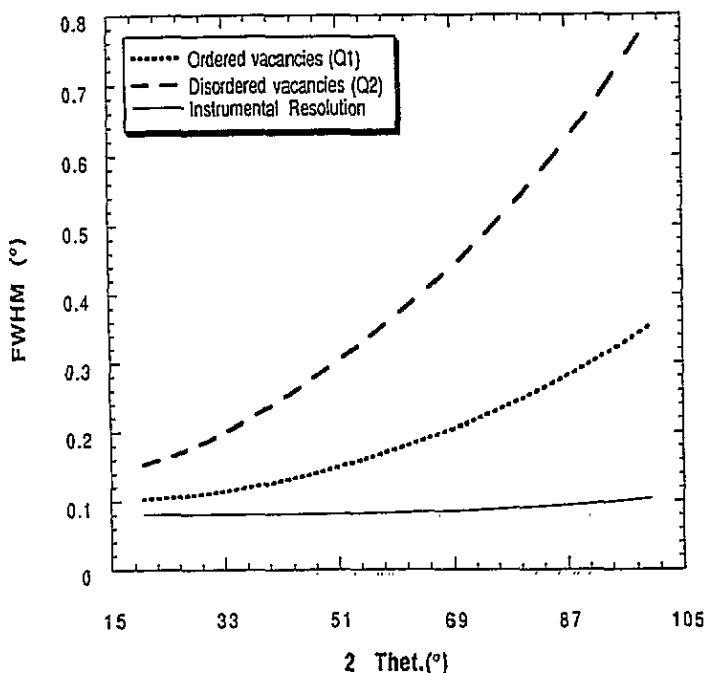
Figure 4. Linewidths for the ordered phase and disordered phase as a function of Bragg angle obtained from the x-ray pattern Rietveld fit.

of Pr are almost unchanged in the two structures. The moments of Pr atoms are found to be parallel to the c axis of the tetragonal cells, with a mean value of $2.0 \pm 0.2\mu_B$, in close agreement with magnetic measurements on a single crystal [4], which gave $2.3\mu_B$. Conversely, Schobinger-Papamantellos *et al* [5] found two different moments on the two crystallographic sites in $PrGe_{1.6}$, one being aligned along the c axis, the other being at some angle from the c axis. We cannot decide from our data whether there are two different moments on the two sites of the ordered structure, but magnetic measurements on the single crystal show a magnetization alignment along the c axis.

5. Discussion

Previous structural studies have been published on the $PrGe_{2-x}$ system ($0.1 < x < 0.5$) by Schobinger-Papamantellos *et al* [5]. At variance with the present work, they always observe a unique phase, the structure of which is orthorhombic (space group $Fdd2$), with $a' \simeq \sqrt{2}a(ThSi_2)$, $b' \simeq 3\sqrt{2}a(ThSi_2)$, $c' = c(ThSi_2)$. In particular, they do not observe in their x-ray study superstructure reflections corresponding to our observation, but they observed faint superstructure lines corresponding to the wavevector $(\frac{1}{3}, \frac{1}{3}, 0)$ in neutron diffraction experiments. An important feature in their measurements is the rapid variation of lattice parameters a and c in the vicinity of $x = 1.7$. A comparison between their data and the values obtained for the ordered and disordered phase of our samples (table 1) shows that we have the following correspondences: the ordered phase with superstructure is the phase with the lower Ge content; the disordered phase has the larger Ge content.

Our experiments performed on the critical composition show without ambiguity (figure 2) that there really are two different phases in equilibrium, which differ by vacancy ordering.

A small increase in the concentration of vacancies induces an order of these vacancies, a contraction in the basal plane and an elongation along the c axis. This behaviour is probably linked to the geometry of the Ge sublattice, with a relaxation of bonds related to a selective repartition of vacancies.

The analysis of linewidth variation with Bragg angle (figure 4) shows that the coherence length is much larger for the ordered structure. The line broadening may be related to the existence in the grains of a gradient of the relative Ge/Pr composition or/and to size and distortion effects, which are expected to be larger for the disordered phase. The observation that the linewidth for (200) lines follows the same law as other lines rules out, within experimental precision, the possibility of large orthorhombic distortion for both phases (when described in the basic ThSi$_2$ cell).

It would be interesting to follow the temperature dependence of linewidths and the evolution of the phase proportions as a function of temperature, starting with a virgin sample. This will be undertaken using high-resolution synchrotron x-ray diffraction.

It is worth comparing the Pr germanide behaviour with those of CeGe$_{2-x}$ and RESi$_{2-x}$ (RE = Ce, Pr) systems, which also exhibit phase separations. For silicides, this phase separation occurs below room temperature near 200 K [1, 2]. It appears that some kind of ordering of Si vacancies occurs at least for one phase. Such ordering has been observed for CeSi$_{1.85}$ by electron diffraction at low temperature, with a superstructure $a' = 7a$(ThSi$_2$). For PrSi$_{2-x}$ the initial tetragonal phase is separated into two phases; one shows a small orthorhombic distortion, which corresponds to a selective repartition of vacancies on one of the two Si sites. The relative proportion of the two phases is stable below 100 K, and rather independent of the sample and of its thermal history for both compounds; it is about 2:1 for CeSi$_{2-x}$ and 3:1 for PrSi$_{2-x}$, the major phase at low temperature (with smaller c) being ordered.

The thermal variation of the c parameter of the disordered high-temperature phase was found to be anomalous between the temperature where phase separation begins and that where the proportion of the two phases is stabilized. This suggests that the ordered phase has a smaller Si content, and that the proportion of Si increases in the disordered phase as the phase separation progresses.

At variance, the phase separation in germanides occurs at temperatures much higher than room temperature, thus the proportion of phases is almost stabilized and no anomalous thermal dilatation is observed. For instance, lattice parameters for PrGe$_{1.6}$ at 25 K are $a = 4.189(2)\sqrt{2}$ Å, $b = 4.189(2)3\sqrt{2}$, $c = 14.06(1)$ Å for the ordered phase, $a = 4.223(3)$ Å, $c = 14.00(1)$ Å for the disordered phase, which are not very different from room temperature data (table 1). However, mechanical treatment and ageing may induce change in the relative proportion of each phase.

Turning now to magnetic properties, both PrGe$_{2-x}$ phases are ferromagnetic with the moment direction along the c axis, thus we cannot clearly distinguish whether there is some difference between the values for the ordered moment in the two phases or not, nor which phase has the highest Curie point. This is different from the CeGe$_{1.6}$ case, where one phase is ferromagnetic, the other being antiferromagnetic.

6. Conclusion

Ordering of vacancies seems to be responsible for the phase separation in light rare earth

silicides and germanides. For silicides, it results from a solid state phase separation, the phase with lower Si content having ordered vacancies. For germanides, similar phase separation occurs. However, it appears at much higher temperature and could not be directly observed, thus its exact mechanism is still unknown.

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