Journal of Alloys and Compounds 320 (2001) 87–92
Journal of ALLOYS AND COMPOUNDS
www.elsevier.com/locate/jallcom

On the stability of hexagonal Ge_7Nb_{10}

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Received 21 November 2000; accepted 4 December 2000

Abstract

Our studies on the Ge–Nb system reveal the existence of a hexagonal compound with the composition Ge_7Nb_{10} that is stable with respect to disproportionation and which was found to crystallize in the space group *P6₃/mmc*. A hexagonal phase of the approximate composition Ge_3Nb_5 has been mentioned by different authors but has been commonly regarded as C- or N-stabilized and therefore not included in the binary phase diagram. A single crystal X-ray study of the compound revealed a Mn_5Si_3-type based structure where half of the *2b* interstitial positions are filled with Ge. X-ray powder diffraction studies and electron probe microanalysis were used to determine the composition ranges of the phases. Various experiments were carried out in order to confirm the thermodynamic stability of this compound and to rule out stabilization by hetero-elements. These studies included the use of different starting materials, different sample preparation techniques and different annealing procedures. The results show strong indications, that Ge_7Nb_{10} is formed as a binary phase which is stable with respect to disproportionation and should therefore be included in the binary phase diagram.

Keywords: Ge–Nb system; Phase diagram; X-ray diffraction

1. Introduction

Compounds with the composition M_5X_3 (M=transition metal, X=Si, Ge) are very common, especially for the early transition metals of the periodic system. Most of these compounds exhibit extremely high thermal stability and some of them (Ti_5Si_3, Mo_5Si_3) are currently investigated for their potential as high temperature materials [1,2]. The M_5X_3 compounds are known to crystallize either in the tetragonal Si_3W_5-type structure ($D8_m$) or in the hexagonal structure type Mn_5Si_3 ($D8_8$). The hexagonal Mn_5Si_3 structure type is in a certain way unique, as it exhibits a preformed cavity capable to bind interstitial (impurity-) elements like B, C, N or O [3]. This feature of the Mn_5Si_3 structure was originally observed by Nowotny and coworkers who found that many binary Mn_5Si_3-type phases in fact required a certain amount of interstitial impurity element for stabilization (e.g. [4–6]). Compounds with this characteristic thus later became labeled 'Nowotny phases'. However, it has been pointed out in a recent report on interstitial binding in Mn_3Si_3-type compounds by Corbett et al. [3], that only some of the phases require interstitial stabilization, while others can well be prepared under clean conditions.

In the Ge–Nb system, two different phases with the approximate composition Ge_3Nb_5 have been described. While there is no discussion of the existence of tetragonal Si_3W_5-type Ge_3Nb_5, there have been controversial reports on a second, hexagonal phase in this composition range. Searcy and Orr [7] reported the existence of two phases with the compositions $NbGe_{0.67\pm0.05}$ (Si_3W_5-type) and $NbGe_{0.54\pm0.05}$ (Mn_5Si_3-type) in the respective composition areas. The authors claimed that the Mn_5Si_3-type phase may be stabilized by carbon impurities introduced during sample preparation and quoted similarities to the Mo–Si system, but the effect of carbon on the stability of the compound was not studied in detail. The Ge–Nb phase diagram was later given by Pan et al. [8] who included (besides the phases Ge_2Nb and $GeNb_3$) the two phases Ge_3Nb_5 and Ge_2Nb_3 in their phase diagram. The authors did not give any information on crystal structures, but based on the stoichiometry the identification of Ge_3Nb_5 with $NbGe_{0.67\pm0.05}$ (Si_3W_5-type) and of Ge_2Nb_3 with $NbGe_{0.54\pm0.05}$ (Mn_5Si_3-type) seems to be justified. According to [8], Ge_3Nb_5 melts congruently at 2150°C, while Ge_2Nb_3 melts in a peritectic reaction at 2040°C. In a later phase diagram study, Jorda et al. [9] claimed that the

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0925-8388/01/$ – see front matter
PII: S0925-8388(00)01499-7

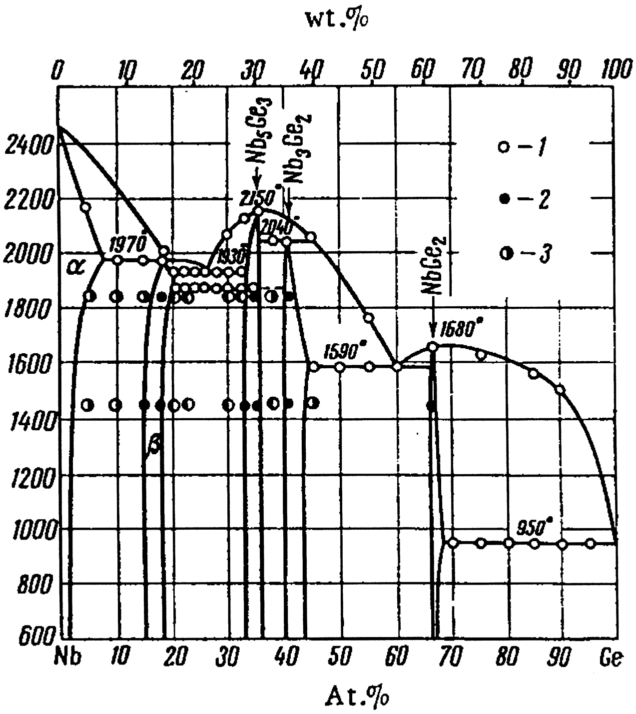

Fig. 1. Ge–Nb phase diagram according to Pan et al. [8].

hexagonal Mn_5Si_3-type phase has to be impurity stabilized and excluded it from their phase diagram. The congruent melting point of Si_3W_5-type Ge_3Nb_5 was found to be 2180°C, in good agreement with Pan et al. While Spear and Palino [10] still included the Mn_5Si_3-type phase in their assessed Ge–Nb phase diagram, later phase diagram versions, e.g. in Massalski's compilation [11] followed the arguments of Jorda et al. [9] and excluded the respective hexagonal phase from the phase diagram. Figs. 1 and 2 are showing the conflicting versions of the Ge–Nb phase diagram according to Pan et al. [8] and Massalski et al. [11].

2. Experimental

Samples of the original sample series were prepared from germanium powder (99.999%, Alfa Aesar) and niobium powder (99.8%, Alfa Aesar) with impurity levels of 1200 ppm oxygen and 160 ppm nitrogen according to the producers certificate of analysis. The powders were handled only in an argon filled glove box during sample preparation. Weighed amounts of the powders were mixed carefully, pressed into 8-mm pellets under a load of 4

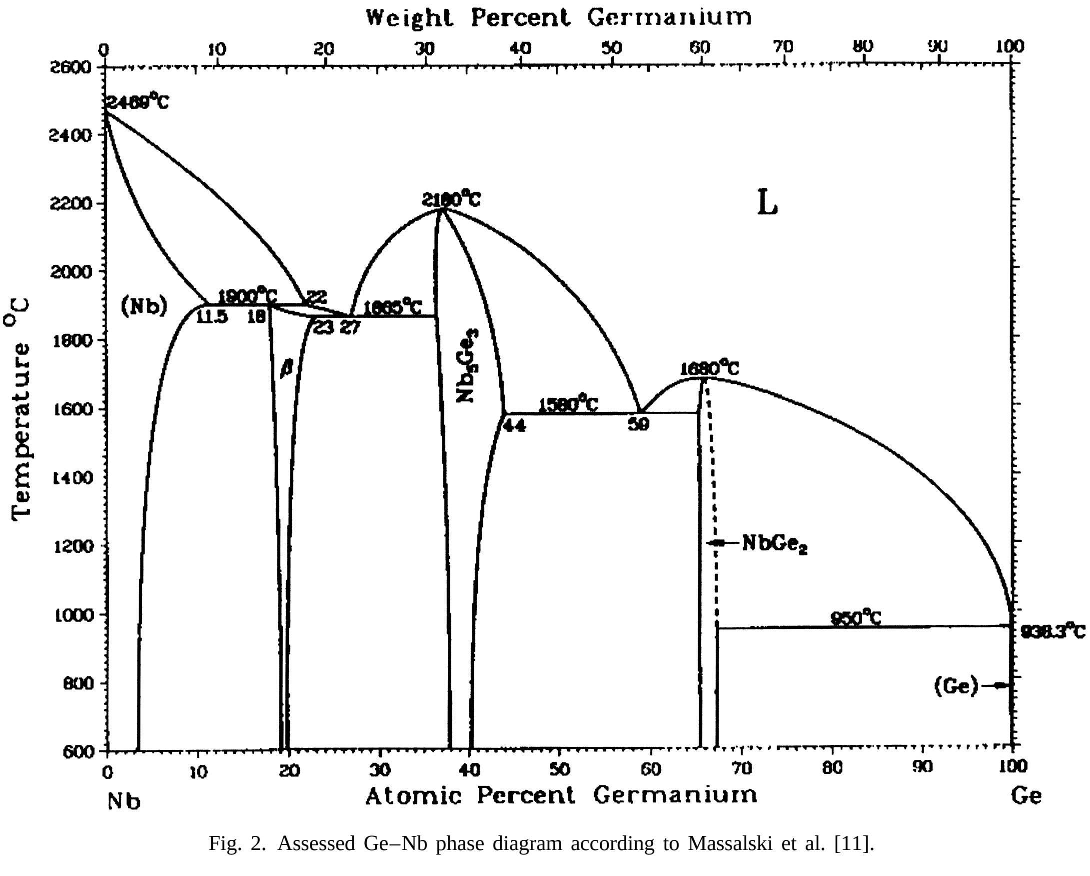

Fig. 2. Assessed Ge–Nb phase diagram according to Massalski et al. [11].

metric tons and then arc-melted on a water-cooled copper hearth under an argon atmosphere. Zr was used as getter material during arc melting. The obtained reguli with a total mass of about 1000 mg were remelted twice for homogenization and then weighed in order to check for possible mass losses. Weight losses of 1–2.5% during the arc-melting process occurred only at the germanium rich side of Ge_3Nb_5 and were attributed to the evaporation of germanium. For equilibration and crystal growth the reguli were subsequently annealed for 10–20 h by induction heating in a tungsten crucible at 1300–1350°C under a dynamic vacuum of $P<2.10^{-6}$ Torr. Selected samples were also annealed at temperatures up to 1600°C, but the evaporation of Ge, and therefore the shift in composition during annealing, was found to be very strong at these high temperatures. As samples of this first series clearly showed the existence of the hexagonal phase, sample preparation procedures were systematically varied in order to rule out possible sources of stabilizing hetero-elements. This included the use of high purity niobium rod (99.99%+, MRC, MARZ grade) with impurity levels of 15 ppm oxygen, 25 ppm carbon and <5 ppm nitrogen according to the analysis certificate and high purity Ge lump (99.9999%+, Alfa) as well as special emphasis on very clean handling and the monitoring of the phase composition of the samples before annealing (arc only). A different series was annealed in closed and evacuated quartz glass ampoules at 1100°C for 3 weeks in order to avoid Ge evaporation during annealing. The respective sample preparation procedures of the individual samples are listed in Table 1 together with experimental results. All experiments, however, regardless of the actual sample preparation procedure, did not yield substantially different results (compare Section 3).

Samples were characterized by means of Guinier powder X-ray diffraction using CuKα radiation and employing high purity silicon as internal standard. The single crystal X-ray diffraction was performed using a Rigaku single crystal diffractometer with MoKα radiation.

Electron probe microanalysis (EPMA) was performed on a Cameca SX electron probe 100 using wavelength dispersive spectroscopy (WDS) for quantitative analyses and employing pure niobium and germanium as standard materials. The measurements were carried out at 15 kV using a beam current of 20 nA. Conventional ZAF matrix correction was used to calculate the final compositions from the measured X-ray intensities.

3. Results and discussion

Table 1 gives an overview of 12 representative samples covering the composition range of interest in the system Ge–Nb and prepared and annealed with varying procedures. The table includes nominal compositions, prepara-

Table 1
Results from X-ray powder diffraction

Sample no.	Nominal composition[a] (at.% Nb)	Preparation procedure[b]	Phase composition
1	66	B, in quartz, 1100°C	Ge_3Nb_5 (main) $GeNb_3$
2	62.5	A, induction heating, 1350°C	Ge_3Nb_5 (main) $GeNb_3$ (trace)
3	62.5	B, in quartz, 1100°C	Ge_3Nb_5 (pure)
4	60.5	B, in quartz, 1100°C	Ge_3Nb_5 Ge_7Nb_{10}
5	60	A, induction heating, 1300°C	Ge_3Nb_5 (main) Ge_7Nb_{10}
6	58.8	B, in quartz, 1100°C	Ge_7Nb_{10} (main) Ge_3Nb_5 (trace) Ge_2Nb (trace)
7	57.5	B, induction heating, 1350°C	Ge_7Nb_{10} (main) Ge_3Nb_5
8	56.5	A, in quartz, 1100°C	Ge_7Nb_{10} (main) Ge_2Nb
9	55	B, arc only	Ge_7Nb_{10} (main) Ge_2Nb
10	55	B, induction heating, 1350°C	Ge_7Nb_{10} (main) Ge_3Nb_5 (trace)
11	50	B, in quartz, 1100°C	Ge_7Nb_{10} Ge_2Nb
12	50	A, arc only	Ge_7Nb_{10} Ge_2Nb

[a] Real composition probably shifted towards higher Nb contents due to evaporation of Ge during arc melting and annealing.

[b] General preparation procedure: A, from powder pellets; arc melting; B, from high purity bulk elements; arc melting.

tion procedures and phase compositions found by Guinier powder diffraction.

A summary and interpretation of the results listed in Table 1 is given below

- The tetragonal phase Ge_3Nb_5 does exist at the stoichiometric composition (62.5 at.% Nb) and can be prepared entirely pure without much difficulty. This is consistent with the congruent melting point of Ge_3Nb_5 reported previously [8,9].
- There is a clear and consistent correlation between the sample composition and the occurrence of the hexagonal phase designated as Ge_7Nb_{10} in Table 1. The phase does not exist at stoichiometric 3:5 composition (62.5 at.% Nb) or at the Nb-rich side of this composition. The hexagonal phase could be prepared almost pure (sample 6 in Table1), showing only traces of Ge_3Nb_5 and Ge_2Nb at a nominal composition of 58.8 at.% Nb. The impurity traces may be due to the incongruent melting of the hexagonal phase reported in [8].
- We could not find a correlation between the occurrence of the hexagonal phase and the purity of our starting materials as stated in Table 1. High purity starting materials and very pure preparation conditions could not suppress the occurrence of the hexagonal phase.
- There is a difference in phase composition between samples annealed at 1300°C under dynamic vacuum and samples annealed in closed quartz tubes at 1100° (e.g. between samples 7 and 8 in Table 1). This difference can be understood by the fact that considerable losses of Ge giving rise to shifts in the overall compositions have been observed during induction heating under dynamic vacuum. As an example compare the phase compositions of samples 9 (arc only) and 10 (after induction heating). A similar Ge loss obviously does not occur during annealing in closed quartz tubes.
- Lattice parameters of the phase Ge_7Nb_{10} in equilibrium with tetragonal Ge_3Nb_5 do not differ significantly from the lattice parameters of the phase in equilibrium with Ge_2Nb. At 1100°C and high purity starting materials the respective values are $a=7.787(1)$ Å, $c=5.392(1)$ Å at the Nb-rich side (sample 4) and $a=7.787(1)$ Å, $c=5.391(1)$ Å at the Ge-rich side (sample 11). This fact indicates a rather limited homogeneity range of Ge_7Nb_{10}.

In summary, our powder diffraction results suggest the existence of a stable hexagonal compound with a composition deviating considerably from the 3:5 stoichiometry. An additional experiment was performed in order to prove that the adopted structure is connected with the composition rather than with impurity levels. A master alloy with 56.5 at.% Nb showing the phase composition [$Ge_7Nb_{10}+Ge_2Nb$] was powdered and mixed with a calculated amount of Nb in order to yield a new overall composition of 66 at.% Nb. After arc melting of this sample the hexagonal phase was not observed and the sample had the phase composition [$Ge_3Nb_5+GeNb_3$], consistent with the phase diagram in Fig. 1. It is thus possible to prepare the tetragonal phase from the hexagonal by a simple shift of composition (additional Nb). The experiment gives clear evidence that the picture of a hetero-element stabilized hexagonal phase $Ge_3Nb_5(X)$ in competition with the 'pure' binary tetragonal phase Ge_3Nb_5 is not correct.

It was found that the intensities of the experimental powder patterns varied noticeably from the pattern calculated assuming the Mn_5Si_3-type structure, and we therefore decided to determine the crystal structure of the hexagonal phase by means of single crystal X-ray diffraction. A regular shaped crystal of the approximate size 150×120×100 μm was isolated from an annealed sample with the nominal composition $Ge_{45}Nb_{55}$ (sample 10 in Table 1). Experimental details of the data collection and refinement are given in Tables 2 and 3. Structure solution and refinement was done using the SHELX 97 program package [12].

The structural parameters in Table 3 show that Ge_7Nb_{10} does not correspond to the simple Mn_5Si_3 structure type. The interstitial *2b* position of the Mn_5Si_3-type structure, which is filled with hetero-atoms in Nowotny phases, was found to exhibit high electron density. Since we have eliminated impurity interstitials as a source of stabilization (and since the observed electron density was too high to be explained by light element interstitials) we conclude that these positions are half filled with Ge atoms. The structure of Ge_7Nb_{10} can thus be described as an intermediate between the completely empty Mn_5Si_3-type structure and the Ga_4Ti_5 structure type showing a completely filled *2b* position. Considering the interstitial doping claimed to be necessary for the stabilization of the hexagonal phase, Ge_7Nb_{10} may thus be described as a self doped Mn_5Si_3-type structure. A graphic representation of the structure of Ge_7Nb_{10} is given in Fig. 3. Nb atoms are drawn as dark

Table 2
Selected data collection and refinement parameters[a]

Empirical formula	Ge_7Nb_{10}
Crystal system, space group	Hexagonal, $P6_3/mcm$
Cell dimensions	
a (Å)	7.783(1)
c (Å)	5.388(1)
V (Å^3)	282.7(1)
Formula units Z	1
Absorption correction	Empirical Ψ scan
Reflections collected, unique	1218/140
Parameters refined	15
Extinction coefficient	0.0297
R, R_w for $I>2\sigma(I)$	0.0186, 0.0404
R, R_w for all data	0.0247, 0.0414

[a] $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w(F_o)^2]^{1/2}$, $w=1/[\sigma^2F_o^2+(a\times P)^2+(b\times P)]$.

Table 3
Positional parameters and site occupancies

Atom	Occupation	Symmetry	x	y	z	U_{eq} (Å^2)
Nb1	1.00	*6g*	0.7372(1)	0	0.25	0.011(1)
Nb2	1.00	*4d*	2/3	1/3	0	0.004(1)
Ge1	1.00	*6g*	0	0.3914(1)	0.25	0.005(1)
Ge2	0.52	*2b*	0	0	0	0.008(1)

circles and Ge atoms as bright circles in Fig. 3. The half filled *2b* Ge-positions are situated in the center of trigonal antiprisms of Nb forming condensed chains along the c axis while the fully occupied *6g* Ge-positions form zigzag chains along c. The figure emphasizes the metallic network (dark) and the Ge–Ge interaction within the chains (bright).

The structure found for Ge_7Nb_{10} is in excellent agreement with a previous report on the hexagonal phase already published in 1971 by Horyn and Kubiak [13]. These authors used the Weissenberg method for their structure investigation of a single crystal grown by chemical vapor transport. Although Ge self-doping was discussed in this paper, the evidence for a stable binary phase Ge_7Nb_{10} was not followed by later authors. Doubt was due to the preparation method (possibility of a metastable phase) and the quality of refinement [14]. Both arguments, however, do not apply to the current study which was performed on a single crystal obtained from an annealed bulk sample and shows a well refined data set.

The structure of a Ge_7Nb_{10} thin film obtained by a co-evaporation technique was also studied with electron diffraction by Arita et al. [15]. The authors found a trigonal superstructure due to the ordering of Ge and vacancies on the interstitial sites. However, we could not find evidence for this ordering which may be due to the higher annealing temperature of our sample (1300°C). An order–disorder transformation of Ge_7Nb_{10} may exist at lower temperatures.

EPMA measurements were performed on four binary samples annealed in quartz tubes at 1100°C in order to confirm the information on phase compositions gathered by X-ray diffraction. The analysis results listed in Table 4 are the mean values of several point analyses within the respective phase. It is estimated, that the composition data are accurate within ±0.5 at.%. Composition data in Table 4 generally show excellent agreement with X-ray diffraction results. The measured composition range of Ge_7Nb_{10} was found to be rather narrow at 1100°C (58.0–58.4 at.% Nb) and fits well with the calculated composition for stoichiometric Ge_7Nb_{10} (58.8 at.% Nb). Surprisingly, the phase Ge_3Nb_5 was also found to exist in a rather limited composition range at 1100°C (62.1–61.5 at.%). This result is in contradiction to the work of Jorda et al. [9], who reported a composition range of approximately 4 at.% at this temperature. However, it fits well with the rather small deviations in the lattice parameters found for the tetragonal phase in the current study. The lattice parameters are $a=10.162(1)$ Å, $c=5.140(2)$ Å at the Nb-rich side (sample 1) and $a=10.168(1)$ Å, $c=5.138(1)$ Å at the Ge-rich side (sample 4).

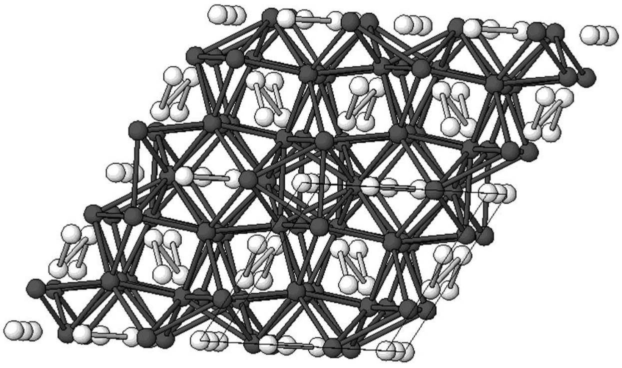

Fig. 3. Structure of Ge_7Nb_{10}, view along [001]. Dark circles: Nb, bright circles: Ge.

4. Conclusions

The preparation of single phase samples in the Ge–Nb system is generally difficult. This is due to the combination of high melting points of the intermediate compounds (requiring high annealing temperatures) with a considerable volatility of Ge in these compounds leading to shifts in the sample composition during the preparation procedure. The incongruent melting of hexagonal Ge_7Nb_{10} makes it even more difficult to prepare this phase pure. In addition there are general doubts concerning the existence

Table 4
Results of EPMA analysis

Sample no.	Nominal composition (at.% Nb)	Phase present	Composition (at.% Nb)
1	66	Ge_3Nb_5	62.1
		$GeNb_3$	79.5
4	60.5	Ge_3Nb_5	61.7
		Ge_7Nb_{10}	58.4
6	58.8	Ge_7Nb_{10}	58.0
		Ge_3Nb_5	61.5
		Ge_2Nb	34.0
11	50	Ge_7Nb_{10}	58.0
		Ge_2Nb	33.6

of truly binary Mn_5Si_3-type phases, as the affinity of this structure to include interstitial hetero-elements like C,N or O is well known. These facts led to the conclusion that the hexagonal phase found in the Ge–Nb system is due to impurities or may be metastable, although the phase has been observed repeatedly by many different authors.

The aim of our study was, to reinvestigate the assumptions that led to the exclusion of hexagonal Ge_7Nb_{10} from the binary phase diagram. We could not suppress the occurrence of hexagonal Ge_7Nb_{10} by variation of preparation route or the use of high purity starting materials. On the other hand, we could show by means of single crystal X-ray diffraction, that Ge_7Nb_{10} is stabilized by germanium self doping at the interstitial sites rather than by interstitial hetero-atoms. X-ray diffraction and EPMA analysis gave a consistent picture of existence and composition range of Ge_7Nb_{10}. Annealing experiments showed the great influence of Ge evaporation during heat treatment. Annealing of Ge_7Nb_{10} under dynamic vacuum will always lead to a shift of composition towards the Ge-poor tetragonal phase Ge_3Nb_5 and ultimately to the complete disappearance of Ge_7Nb_{10}. This may give rise to the misinterpretation, that Ge_7Nb_{10} is a metastable phase.

Based on our study we thus propose to reassess the Ge–Nb system and to include the phase Ge_7Nb_{10} into the phase diagram as was done in the original work by Pan et al. [8] shown in Fig. 1.

Acknowledgements

Klaus Richter thanks the Austrian Science Foundation (FWF) for an Erwin-Schrödinger-Scholarship (J1557-CHE). This research was supported by the Office of the Basic Energy Science, U.S. Department of Energy. The Ames Laboratory is operated by the DOE under the contract No. W-7405-Eng-82.

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