AD-752 877

A PHASE EQUILIBRIUM DIAGRAM FOR THE VANADIUM-GALLIUM SYSTEM

V. M. Pan

Naval Research Laboratory
Washington, D. C.

4 December 1972

A PHASE EQUILIBRIUM DIAGRAM FOR THE VANADIUM-GALLIUM SYSTEM

(Diagramma ravnovesiya faz sistemy vanadiy-galliy)

by V.M. Pan

D D C

DEC 21 1972

B

A PHASE EQUILIBRIUM DIAGRAM FOR THE VANADIUM-GALLIUM SYSTEM (*)

by V.M. Pan

One of the most promising materials for superconducting solenoids is the intermetallic compound V_3Ga. This compound was first studied in the works of Matthias et al. [1, 2], where it was shown to have a crystal structure of the β-W type (a = 4.816Å), and that the temperature of its transition to the superconducting state (T_c = 16.5°K) reported by Roberts [13] is thought to be more accurate.

It was shown in [4] that, when the composition of intermetallic V_3Ga differs from stoichiometry, the superconducting transition temperature T_c decreases. For a component ratio in the alloy of V/Ga = 2, T_c = 7.6°K, and for a ratio of V/Ga = 4, T_c = 10.1°K. The authors of [2] note that, according to their observations, the crystal lattice parameter of V_3Ga does not change when the ratio of V/Ga is changed from 3 to 5.

A small amount of the second phase was discovered in all the alloys, but in the alloy with a ratio of V/Ga = 2 a third phase was also found. The nature of these phases has not been established. The work of Schubert et al. [5] indicates the existence of a compound V_2Ga_5, with a tetragonal structure of the Mn_2Hg_5 type (space group P4/mbm and parameters a = 8.96_3Å and c/a = 0.300). The existence of a V_2Ga_5 compound with a structure of the Mn_2Hg_5 type was confirmed in [6-8]; in [6], the following parameters were obtained for the unit cell:
a = 8.9723 ± 0.0002Å, c = 2.6895 ± 0.0003Å, c/a = 0.300 and a density of 6.90 ± 0.05 g/cm^3; according to [7], a = 8.98_5Å and c = 2.69_6Å.

In both works, it was shown that the compound V_2Ga_5 decomposes at

$1085 \pm 5°C$ with a peritectic reaction, into a liquid rich in gallium and another compound containing approximately 50 at% Ga. According to the data of [6], this compound contains 52 ± 2 at% Ga, has a formula of V_6Ga_7, and a bcc crystal structure with a lattice parameter of $a = 9.17$ Å; it is of the γ-phase type, belonging to the Hume-Rothery phases with an e/a ratio of 21/13. (The same structure was found for this compound by Schubert et al. [9], but there it was assigned the formula VGa.) This compound is stable at temperatures above $995 \pm 5°C$. At lower temperatures, it decomposes into V_2Ga_5 and another compound with 46 ± 2 at% Ga. The latter is stable down to room temperature; it has a formula of V_6Ga_5 and a crystal structure, apparently, of the Ti_6Sn_5 type, which may be described as a hexagonal unit cell with the parameters $a = 8.496 \pm 0.001$ Å, $c = 5.174 \pm 0.001$ Å, and $c/a = 0.61$. It should be noted that neither V_6Ga_7 nor V_6Ga_5 were obtained in the single phase state by the authors of [6].

According to [7], five intermetallic compounds exist in V-Ga alloys: V_3Ga, V_5Ga_3, VGa, V_2Ga_5, and still another compound with a higher Ga content. All of these compounds are formed from liquid by peritectic reactions at the following temperatures: 1525, 1195, 1110, 1080 and $485°C$, respectively. The compound V_5Ga_3 decomposes at a temperature of about $935°C$ into V_3Ga and VGa. The authors of [7] believe that the structure of the compound VGa represents a superstructure of the α-Fe [sic] type (the period of the substructure is $a = 3.01_5$Å).

This work presents a phase equilibrium diagram of the vanadium-gallium system; the diagram is more detailed in the range of concentrations where the compound V_3Ga exists.*

For these studies, 35 alloys were prepared from vanadium (99.5) and gallium (99.999) in an arc furnace with a tungsten electrode and a watercooled copper hearth in an argon atmosphere. The alloys were

---

* After the present work was completed, there appeared a report of the work of Van Vucht et al. [8], in which a phase diagram of the V-Ga system was also constructed. The high-V part of the diagram in [8] coincides with ours.

prepared in 10g charges, and it was found that the weight of an ingot practically did not differ from the sum of the weights of its components. Therefore, we assumed that the composition of the alloy corresponds to that of the charge. In general, this was confirmed by chemical analysis. The alloy compositions are given in the table.

Alloy No.	Composition				α phase		β phase	
	by mix		by anal.		Lattice parameter, Å	microhardness, kg/mm²	Lattice parameter, Å	microhardness, kg/mm²
	Ga, wt %	Ga, at %	Ga, wt %	Ga, at %				
1	0	0	—	—	$3{,}027_7$	276	—	—
2	10	7,51	—	—	$3{,}034_2$	343	—	—
3	20	15,45	—	—	$3{,}039_4$ (1300°) $3{,}035_2$ (900°)	448	$4{,}801_4$	802
4	23	22,13	—	—	$3{,}040_4$	479	$4{,}805_3$	906
5	30	23,85	—	—	—	—	$4{,}806_7$	906
6	31,3	25,0	—	—	—	—	—	852
7	32	25,59	—	—	$3{,}043_1$	513	$4{,}809_7$	852
8	34	27,35	—	—	—	513	$4{,}809_2$	878
9	36	29,13	—	—	$3{,}044_1$	—	$4{,}812_2$	878
10*	36	29,13	35,5	28,68	—	—	—	—
11	38	30,93	—	—	—	539	$4{,}813_7$	852
12	40	32,76	—	—	$3{,}046_1$	539	$4{,}813_2$	906
13	42	34,60	41,3	34,42	$3{,}048_7$	528	$4{,}814_2$	—
14	44	36,48	45,8	37,57	$3{,}050_1$	—	—	—
15	45	37,42	—	—	—	—	—	—
16	46	38,37	47,5	39,8	—	—	—	—
17	48	40,28	48,2	40,48	—	—	—	—
18	50	42,22	50,5	42,71	—	—	—	—
19	50	42,22	49,9	42,13	—	—	—	—
20	50	42,22	50,7	42,91	—	—	—	—
21	52	44,18	52,4	44,58	—	—	—	—
22	54	46,17	53,4	45,58	—	—	—	—
23	55	47,18	54,5	46,68	—	—	—	—
24	56	48,19	56,0	48,19	—	—	—	—
25	60	52,29	58,5	50,75	—	—	—	—
26	60	52,29	61,8	54,18	—	—	—	—
27	62	54,39	63,4	55,87	—	—	—	—
28	65	57,58	69,2	62,10	—	—	—	—
29	70	63,03	72,9	66,29	—	—	—	—
30	75	68,68	78,3	72,51	—	—	—	—
31	75	68,68	75,8	69,6	—	—	—	—
32	80	74,51	—	—	—	—	—	—
33	85	80,55	—	—	—	—	—	—
34	90	86,80	—	—	—	—	—	—
35	95	93,28	—	—	—	—	—	—
36	98	97,28	—	—	—	—	—	—
37	100	100	—	—	—	—	—	—

* Alloy prepared with high-purity vanadium.

The cast alloys were studied by microstructural and X-ray analysis. Subsequently, alloys nos. 2 to 29 were annealed at 900°C. The duration of anneals for the different alloys ranged from 40 to 100 hours. The specimens to be annealed were sealed in quartz ampoules, which were evacuated and then filled with argon. After the anneal the specimens were quenched in water by breaking the ampoules.

Since the appearance of dendritic segregation sometimes obscures the results in cast alloys, the differential thermal analysis was performed only with the annealed alloys, in an apparatus described in [10].

The alloys, quenched after annealing at 900°C, were studied by microstructural, X-ray and microhardness analysis.

A number of alloys, quenched from various temperatures in the range of 1040 to 1400°C, were subjected to X-ray structural analysis. The quenching was performed in a special vacuum-argon device. Cas'-- oil was used as the quenching medium. The temperature was measured with a W-W+20Re thermocouple. Annealing at the given temperature t. 15 minutes. The quenching was performed with either solid specimens or powders of the alloys to be investigated. The powders were prepared by crushing in a special mortar or by filing (depending on the mechanical properties of the alloys). The powders were placed in thin-walled Mo containers with covers and loaded into the quenching apparatus.

X-ray photographs were made with rotating powder specimens in a cylindrical camera with a diameter of 57.3 mm, using unfiltered Cr radiation.

The specimens for microstructural analysis were prepared by mechanical polishing on a cloth wet with a water suspension of chromium oxide. The specimens were etched in a reagent with the following composition: 1 part HF, 2 parts HNO_3, 5 parts HCl and 20 parts of H_2O. The microhardness was measured in a PMT-3 device with 50g pressure.

As a result of these studies, a phase equilibrium diagram of the V-Ga system was constructed as shown in Fig. 1. The shape and position
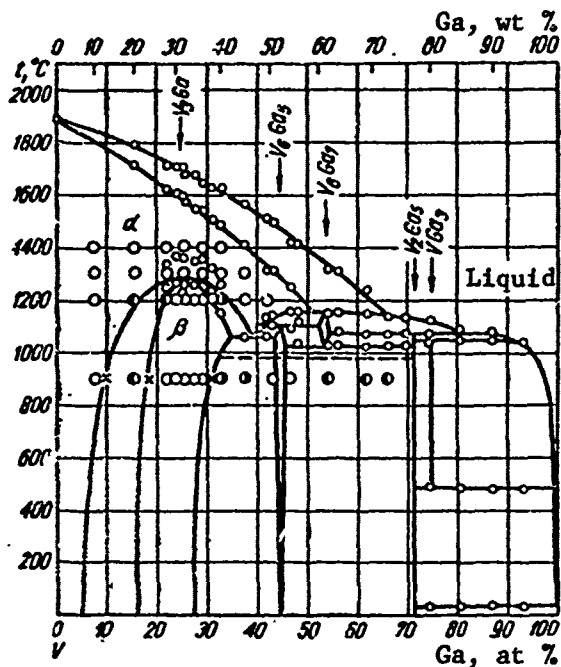
Fig. 1: Diagram of phase equilibrium of vanadium-gallium
system: o-thermal analysis: O-one phase; ⊙-two
phases; x-solubility, determined by measuring the
lattice parameter.

of the solidus and liquidus curves, and also the position of all hori-
zontals corresponding to three-phase nonvariant equilibria, were
determined by differential thermal analysis, while the temperatures
were determined from the heating curve. Eight phases were discovered
in alloys of the vanadium-gallium system in the solid state: α phase -
a solid solution of Ga in V; β phase - a solid solution based on the
intermetallic compound V_3Ga; γ phase - the intermetallic compound
V_6Ga_7; δ and δ' phases - high temperature and low temperature modifi-
cations of the intermetallic V_6Ga_5; ε phase - intermetallic V_2Ga_5;
η phase - intermetallic VGa_3; and the ζ phase - gallium.

We have shown that the solid solution of Ga in V forms a broad
single-phase region, where the limiting solubility of Ga in V is
approximately 50-51% at a temperature of 1145°C. This value for the
limiting solubility was determined from the intersection of the

- 5 -

solidus curve bounding the α and α+liquid regions with the horizontal of the three-phase nonvariant peritectic equilibrium α ⇄ 1̣ ·   γ at 1145°C.
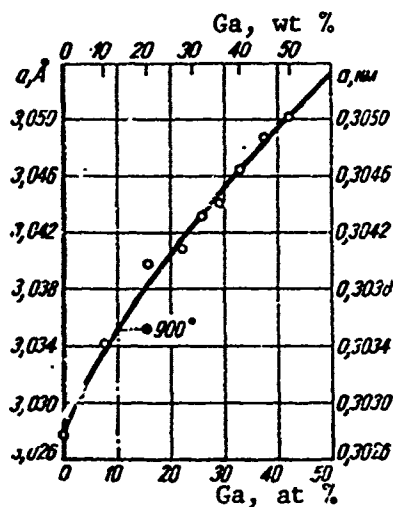

Fig. 2.   Crystal lattice parameter of α-solid solution
          as a function of composition.

Alloying with Ga causes the bcc lattice parameter of vanadium to increase from 3.028 ± 0.002 Å for pure V to 3.053 ± 0.002 Å for 50% Ga.* In the curve representing the change in the lattice parameter (Fig. 2), a positive deviation from the additive rule was observed. It should be noted that we studied the parameter change in the powders of the alloys quenched from 1200, 1300 and 1400°C. Our measurement of the parameter of the α solution in alloy no. 3 (15.45% Ga), which was quenched after annealing at 900°C and revealed a two phase α + β structure, showed that the solubility of Ga in V at 900°C is 10%.

We have shown that intermetallic V_3Ga is formed in the solid state from the α-solid solution. The nonvariant α ⇄ β equilibrium takes place at a temperature of about 1280°C near the stoichiometric

---

* Close values for the crystal lattice parameter of V were found by
  other authors: 3.0282 ± 0.0001 Å [11], 3.0278 ± 0.0001 Å [12].

composition of V_3Ga. It should be noted that in the thermal analysis curves of the alloys which are close to the V_3Ga composition (nos. 4 to 10), the thermal effect of the $\beta \rightarrow \alpha$ transformation extended over approximately $100°$ (even for the stoichiometric composition); it begins at $1250-1260°C$ and ends at $1350-1360°C$. The rate of heating was approximately 40-50 degrees/minute. It was shown by X-ray structural analysis of alloys no. 3-12, quenched from a temperature of $1300°C$, that only the solid α solution exists at this temperature in this range of alloy compositions. Therefore, we concluded that the temperature of the end of the $\beta \rightarrow \alpha$ transition determined by differential thermal analysis was nonequilibrium.

It was discovered that the α-solid solution, in the range of Ga concentrations of approximately 35 to 44%, dissociates upon cooling by a eutectoid reaction. The temperature of the three-phase nonvariant eutectoid equilibrium $\alpha \rightleftarrows \beta+\delta$, determined from the thermal analysis curves of alloys nos. 14 to 21, is $1060°C$. The eutectoid point lies approximately at 39% Ga.

We measured the lattice parameter of intermetallic V_3Ga in alloys quenched after annealing at $900°C$. It was shown that, when the Ga concentration was changed from 18.4 to 30.8%, the lattice parameter increased from 4.802 ± 0.001 Å to 4.814 ± 0.001 Å (Fig. 3). For Ga concentrations less than 18.4% and more than 30.8%, the parameter remains constant. Thus at $900°C$, the width of the single phase β region is 12.4%. At $1065°C$ it equals approximately 15%, and at $1200°C$, it is about 9%. The microhardness of the β phase is practically independent of composition and equals 850-900 kg/mm^2.

On the heating curves for alloys nos. 25 to 28, a thermal effect is observed at $1145°C$; its magnitude reaches a maximum in alloys no. 26 and 27. X-ray structural analysis of alloys nos. 18 to 28, quenched from 1130 and $1140°C$, showed that this thermal effect accompanies the formation of an intermetallic compound which we will designate as V_6Ga_7, following the authors of [6 and 8]. The X-ray
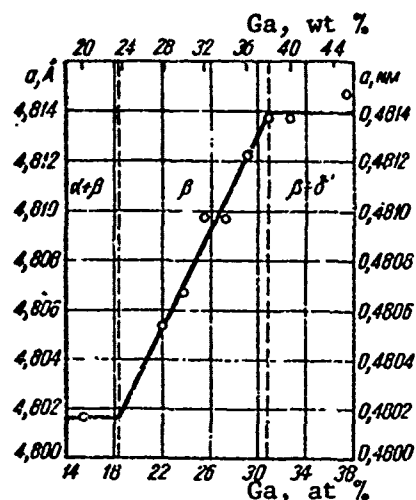
- 7 -

Fig. 3. Crystal lattice parameter of the β phase as a function of composition in alloys quenched after annealing at 900°C.

photograph of this compound is indexed with the assumption that its structure is an ordered bcc solid solution of the γ-brass type with the parameter a = 9.166 Å. This parameter corresponds to a tripled parameter of the initial α solution with a = 3.055 Å. It is interesting that extrapolation of the curve a = f(c) for the α solution, shown in Fig. 2, up to a value of c = 53.75% Ga, i.e., up to the stoichiometric composition of V_6Ga_7, gives a value for the parameter of a = 3.055 Å.

The compound V_6Ga_7 exists in a narrow temperature range. Forming at 1145°C, it decomposes at 1030°C by the eutectoid reaction γ → δ + ε. A thermal effect is observed at 1030 ± 20°C on the heating curves for alloys nos. 22 to 29 and 31; X-ray structural analysis shows that the γ phase is still present in the alloys quenched from 1040°C, but is not present in the same alloys quenched from 900°C.

The δ phase, which by assumption represents the intermetallic compound V_6Ga_5 [6, 8], was observed by us through X-ray and micro-structural phase analysis in alloys nos. 12 to 29, quenched after annealing at 900°C. According to the data from differential thermal

analysis, we are compelled to assume that this compound is formed in the solid state by the peritectoid reaction $\alpha + \gamma \to \delta$. The thermal effect of the dissociation reaction of this compound was located at 1100 C° on the heating curves for alloys nos. 20 to 25; the greatest magnitude of the effect was seen in alloys nos. 21 and 22.

The δ phase X-ray photograph obtained from alloys nos. 21 and 22, quenched from temperatures of 1040-1130°C, may be indexed with the assumption that it has a hexagonal lattice of the α-Ti_6Sn_5 type [8] with the parameters a = 8.496 Å, c = 5.176 Å and c/a = 0.61. After annealing at 900°C, a series of new lines appear on the X-ray photographs of the δ phase. These lines appear regardless of whether the alloy falls in the δ, $\delta + \beta$ or $\delta + \varepsilon$ regions; the only condition is that there be enough δ phase present in the alloy for the lines to be noticeable. It is possible that the appearance of the new lines on the X-ray photograph may be connected to the appearance of polymorphism in the intermetallic V_6Ga_5. It is probable that V_6Ga_5, like Ti_6Sn_5 [8], forms an orthorhombic modification in addition to the hexagonal form. The X-ray photograph of the assumed low temperature modification of V_6Ga_5 (the δ' phase) has not yet been interpreted.

The intermetallic compound V_2Ga_5 (the ε phase) is formed in the solid state by a peritectic reaction. The temperature of the three-phase nonvariant equilibrium $\gamma + L \rightleftarrows \varepsilon$, determined from the heating curves for alloys nos. 27 to 29 and 31, is 1080°C. The data from differential thermal and X-ray structural analysis confirm that the single-phase region is located between alloys nos. 31 (69.60% Ga) and 30 (72.51% Ga). The apex of the Tamman triangle constructed from the values of the thermal effects of the reaction $\varepsilon \to \gamma + L$ is located in the region of 71-72% Ga. The X-ray photographs of the compound V_2Ga_5 are well indexed with the assumption that it has a tetragonal structure of the Mn_2Hg_5 type with the unit cell parameters a = 8.959 Å and c = 2.690 Å.

The compound VGa_3 (the η phase) is formed by a peritectic reaction. The temperature of the three-phase nonvariant equilibrium

$\varepsilon + L \rightleftarrows \eta$, determined by the method of differential thermal analysis of the heating curves of alloys nos. 30 and 32 to 34, is 1060°C. The special feature of the η phase consists in the fact that it exists only at higher temperatures: from 1060 to 480°C. A three-phase nonvariant reverse peritectic equilibrium, $\eta \rightleftarrows \varepsilon + L$, takes place at 480°C (as determined from the heating curves for alloys nos. 30 and 32 to 35).

The apex of the Tamman triangle constructed from the values for the thermal effects of the reverse peritectic reaction $\varepsilon + L \rightarrow \eta$ lies in the region of stoichiometric composition of VGa_3. It is not possible to construct a Tamman triangle for the values of the thermal effects of the peritectic reaction $\eta \rightarrow \varepsilon + L$. It is also impossible to retain the η phase for room temperature X-ray photography by quenching. Therefore, X-ray structural analysis revealed the $\varepsilon\text{-}V_2Ga_5$ and ζ-Ga phases in alloys nos. 30 and 32 to 35.

As is well known, pure gallium melts at 29.8°C [13]. The temperature of the eutectic equilibrium $L \rightleftarrows \varepsilon + \zeta$ is about 0.05° lower than the melting temperature of Ga.* We may conclude from this that the solubility of V in Ga is negligible.

It should be noted that microstructural analysis of the vanadium-rich alloys (both cast and annealed) revealed a noticeable amount of an additional phase, which is practically not revealed by X-ray structural analysis and which gradually decreases as the Ga concentration increases. Judging from the following certified content of impurities in the initial vanadium: Fe-0.04%, Al-0.01%, Si-0.02%, S < 0.005%, N-0.008%, C-0.04%, O-0.29%, we may suppose that this additional phase is most probably vanadium oxide.

We melted two controlled alloys using vanadium as the charging

---

* The difference between the melting point of Ga and the eutectic in alloy No. 35 (6.72% V) was measured at our request by G.A. Alfintsev of the Institute of Metal Physics of the Academy of Sciences, Ukrainian SSR.

material, purified by electron-beam remelting in a high vacuum (residual pressure 10^{-5}mm Hg). By this purification, the melting point of vanadium is raised by 60° (from 1890 to 1950°C), and the hardness is decreased by more than a factor of two. Microstructural analysis of the control alloys revealed a significant decrease in the amount of the additional phase. Thermal and X-ray structural analysis of the control alloys showed practically complete coincidence of the phase composition and position of the critical points. This supports our assumption that the additional phase does not belong to the vanadium-gallium system.

RESULTS:

1. A phase equilibrium diagram for the vanadium-gallium system has been constructed by means of differential-thermal, quenching-X-ray-structural and quenching-microstructural analysis.

2. Eight phases have been observed in the alloys of the vanadium-gallium system in the solid state: the α-solid solution of Ga in V (maximum solubility about 51% Ga); the β-solid solution based on intermetallic V_3Ga (width of the region of homogeneity at 900°C - 12.4%; at 1065°C - 15%; and at 1200°C - 9%); the γ phase - intermetallic V_6Ga_7; the δ and δ' phases - the high-temperature and low-temperature modifications of intermetallic V_6Ga_5; the ε phase - intermetallic V_2Ga_5; the η phase - intermetallic VGa_3; and the ζ phase - gallium.

3. It was shown that the following nonvariant equilibriums occur in alloys of the vanadium-gallium system: three peritectic reactions, $\alpha + L \rightleftarrows \gamma$ (1145°C; 53.75% Ga), $\gamma + L \rightleftarrows \epsilon$ (1080°C; 71.45% Ga), and $\epsilon + L \rightleftarrows \eta$ (1060°C; 75% Ga); the reverse peritectic, $\eta \rightleftarrows \epsilon + L$ (480°C, 75% Ga); the eutectic, $L \rightleftarrows \epsilon + \zeta$ (29.7°C); two eutectoids, $\alpha \rightleftarrows \beta + \delta$ (1060°C; 39% Ga) and $\gamma \rightleftarrows \delta + \epsilon$ (1030°C; 53.75% Ga), the peritectoid, $\alpha + \gamma \rightleftarrows \delta$ (1100°C; 45.45% Ga); the equilibrium $\alpha \rightleftarrows \beta$ (1280°C, 25% Ga); and the allotropic, $\delta \rightleftarrows \delta'$ (950-1000°C; 45.45% Ga).

- 11 -

REFERENCES

1. Matthias, B.T., et al. Phys. Chem. Solids, 1, 1956, 188.

2. Wood, E.A., et al. Acta Crystallogr., 11, 1958, 604.

3. Roberts, B.W. General Electric Research Laboratory, New York, Tech. Rept. 63-RL-3252M, March, 1963.

4. Blumberg, W.E., et al. Phys. Rev. Letters, 5, 1960, 149.

5. Schubert, K., et al. Naturwiss., 49, 1962, 57.

6. Van Vucht, J.H.N., Bruning, H.A., and Donkersloot, H.C. Phys. Letters, 7, 1963, 297.

7. Savitskiy, Ye.M., et al. Zh. Neorg. Khim., 9, 1964, 1155 [For English translation, see Russian Journal of Inorganic Chemistry, 9, 1964, pp. 631-633].

8. Van Vucht, J.H.N., et al. Philips Research Reports, 19, 1964, 407.

9. Schubert, K., et al. Naturwiss., 50, 1963, 41.

10. Svechnikov, V.N., et al. In the series: "Voprosy fiziki metallov i metallovedeniya" (Problems of the Physics of Metals and Metallography), Izd. AN USSR (Acad. Sci., Ukranian SSR), Kiev, 1962, No. 16, 220.

11. Beatty, S. J. Metals, 4, 1952, 987.

12. Seybolt, A.U., and Sumsion, H.T. J. Metals, 5, 1953, 292.

13. Filyand, M.A., and Semenova, Ye.I. Svoystva redkikh elementov (The Properties of Rare Elements), Metallurgizdat, Moscow, 1953 [For English translation, see: Hand. ok of the Rare Elements, pub. by Boston Technical Publishers, Cambridge, Mass., 1968].