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F.C.C. Solid Solutions in Al-Ge and Al-Si Alloys under High Pressure

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The systems Al-Ge and Al-Si at atmospheric pressure are simple eutectic ones /1/. The terminal (Al) solid solutions are limited to 2.8 at% Ge and 1.6 at% Si, respectively. The small terminal solubility is proper to the metal-semiconductor equilibrium. However, the metallic radii of Ge and Si for coordination number 12 are close to that of Al:  $r_{\text{Ge}} = 0.1369$ ,  $r_{\text{Si}} = 0.1319$ , and  $r_{\text{Al}} = 0.1432$  nm /2/. Thus for Al-Ge and Al-Si the atomic size factors are favourable for the mutual solid solubility. On the other hand, the electrochemical factors are small, because both alloy components belong to the adjacent groups in the Periodic Table. This suggests that extended solid solutions possibly may be formed in Al-Ge and Al-Si systems. In fact, a substantial increase in solubility of Ge and Si in Al has been observed under high pressure /3, 4/ as well as by rapid quenching from the liquid state /5, 6/.

The aim of the present investigation was to determine in detail the solubility limits of Ge and Si in Al at pressures up to 100 kbar and to study the effect of solubility on the f.c.c. (Al) lattice parameter and superconducting properties.

Samples 5 mm in diameter and  $\approx 1$  mm thick were subjected to high pressures and temperatures, then rapidly cooled to liquid nitrogen temperature, and the pressure was released to atmospheric. The crystal structure of the samples was analyzed by the X-ray powder technique at  $-150^{\circ}\text{C}$  using  $\text{CuK}_{\alpha}$  radiation. For a more accurate determination of the f.c.c. lattice parameters, Co radiation was used. The superconducting transition temperature,  $T_c$ , of quenched alloys was measured by the induction technique. Other experimental details are published in /7/. Preparation of sample alloys and some preliminary results are described in /8/.

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Table 1

alloy composition (at%)	treatment conditions		phase present in quenched alloys	lattice parameter, $a$ (nm), at $-150^{\circ}\text{C}$ , $\Delta a = \pm 0.0003$ nm	$T_c$ (K)
	P(kbar)	T( $^{\circ}\text{C}$ )			
Al-3 Ge	45	400	$\alpha$	0.4044	2.0
6 Ge	70	400	$\alpha$	0.4045	3.2
10 Ge	70	400	$\alpha$	0.4053	4.7
15 Ge	70	400	$\alpha$	0.4064	7.2
25 Ge	100	420	$\alpha + \Phi$	0.4069 <sup>*)</sup>	7.0
37 Ge	75	325	$\alpha + \Phi$	0.4068 <sup>*)</sup>	6.9
Al-5 Si	70	500	$\alpha$	0.4034	3.3
12 Si	70	500	$\alpha$	0.4017	5.8
18 Si	90	700	$\alpha$	0.4009	10.6
25 Si	100	650	$\alpha + \text{Si}$	0.4004 <sup>*)</sup>	10.0
35 Si	100	620	$\alpha + \text{Si}$	0.4001 <sup>*)</sup>	11.0
50 Si	100	700	$\alpha + \text{Si}$	0.4004 <sup>*)</sup>	10.3

<sup>\*)</sup> in the presence of another phase.

**Results and discussion** The main results on the crystal structure and the superconductivity of Al-Ge and Al-Si alloys after pressure-temperature treatment are summarized in Table 1 and Fig. 1, 2. Single phase alloys with f.c.c. structure were obtained at 3, 6, 10, 15 at% Ge and 5, 12, 18 at% Si. The f.c.c. lattice parameter  $a$  rises linearly with Ge content from 0.4038 nm for pure Al to 0.4069 nm (at  $-150^{\circ}\text{C}$ ), while that for Al(Si) decreases to 0.4001 nm. The superconducting transition temperature increases from 1.2 K for pure Al to 7.2 K for Al(Ge) and 11.0 for Al(Si) solid solutions. The observed changes in  $a_{\text{f.c.c.}}$  and  $T_c$  (Fig. 1, 2) show that the solubility of Ge and Si in Al under the given treatment condition reaches to  $\approx 18$  at% Ge and  $\approx 20$  at% Si.

In order to enhance the solubility limits, the alloys were subjected to the maximum pressure, 100 kbar, attainable in our high pressure chamber. However, these experiments did not yield single phase alloys. Further extension of the Ge solubility in Al is limited by the formation of an intermediate phase,

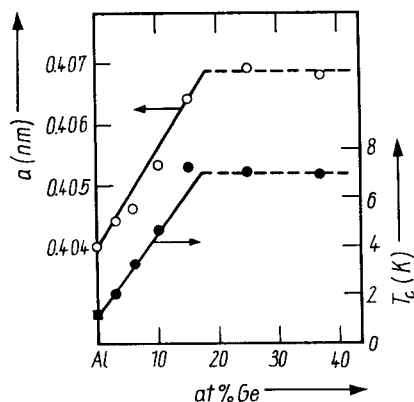


Fig.1

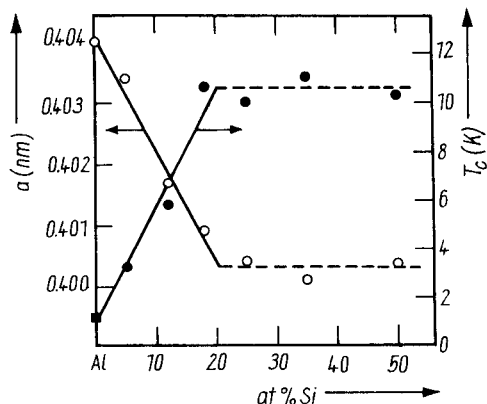


Fig.2

Fig. 1. Lattice parameter (○) and  $T_c$  (●) of Al-Ge solid solutions versus germanium content; (■)  $T_c$  value for pure Al

Fig. 2. Lattice parameter (○) and  $T_c$  (●) of Al-Si solid solutions versus silicon content; (■)  $T_c$  value for pure Al

designated as  $\Phi$ . The crystal structure, properties, and composition of the  $\Phi$ -phase will be described elsewhere. No intermediate phase was found in the Al-Si system at pressure up to 100 kbar.

It is of interest to compare our dependences  $a_{f.c.c.}$  versus solute content with the available literature data on the solubility of Ge and Si in Al at atmospheric pressure [9]. For Al(Ge), a good agreement in the slope  $a_{f.c.c.} = f(c)$  is observed. For Al(Si) the observed rate of  $a_{f.c.c.}$  change with Si content (from 5 to 18 at% Ge) is smaller than that for the equilibrium at 1 bar solid solutions, which exist only at  $c \leq 1.6$  at% Si.

The extrapolation of the  $a_{f.c.c.}(c)$  dependences to germanium and silicon leads to  $a_{Ge} = 0.423$  nm and  $a_{Si} = 0.398$  nm. These lattice parameters correspond to the atomic radii  $r_{Ge} = 0.149$  and  $r_{Si} = 0.141$  nm, which are somewhat greater than the generally accepted metallic radii of Ge and Si for the coordination number 12. We suppose that our values of metallic radii are more suitable for evaluating parameters of the virtual close-packed structures since they are obtained from solid solutions of Ge and Si in aluminium, which is their nearest neighbour in the Periodic Table and has consequently similar inner electron shells, minimum difference in electronegativity, etc. For the silicon

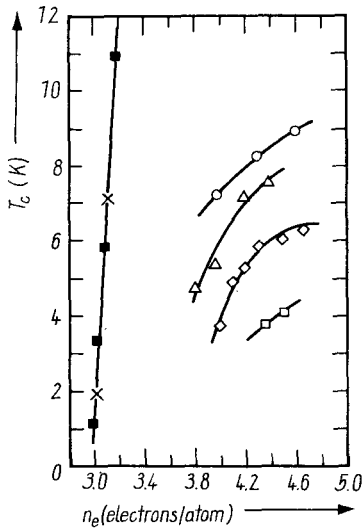


Fig. 3. Dependences of superconducting temperature  $T_c$  on electron concentration  $n_e$  for some alloys of non-transition metals;  $\square$  simple cubic  $\pi$ -phase in In-Sb,  $\diamond$  "hite tin" (" $\beta$ -Sn")-phase in Sn-Bi,  $\Delta$  simple hexagonal  $\gamma$ -phase in In-Bi,  $\circ$  f.c.c. ( $\alpha$ )- and h.c.p. ( $\epsilon$ )-phases in Pb-Bi,  $\times$  f.c.c.  $\alpha$ -phase in Al-Ge,  $\blacksquare$  f.c.c.  $\alpha$ -phase in Al-Si

f.c.c. structure we find good agreement between the relative volume  $V/V_0 = 0.790$  obtained on the basis of our radius and the theoretically calculated one, ranging between 0.797 and 0.694 /10/.

The extension of the Ge and Si solubility in Al results in a drastic increase in the f.c.c. phase superconducting transition temperature. It is of interest to compare the obtained dependence of  $T_c$  on the electron concentration,  $n_e$ , with that for other phases in the alloys of non-transition metals formed under high pressure /11/. The family of  $T_c(n_e)$  curves presented in Fig. 3 shows a number of significant features. First, the  $T_c$  value of either phase increases smoothly with  $n_e$  within the concentration range where a given phase exists. It is in agreement with the known empirical Matthias rule for non-transition metals. Second, as we go over to some other phase with closer packed structure (greater coordination number) in the sequence

$$\pi(6) \rightarrow \text{"}\beta\text{-Sn"}(4+2) \rightarrow \gamma(\approx 8) \rightarrow \epsilon, \alpha(12),$$

the corresponding  $T_c(n_e)$  curve shifts to higher  $T_c$  values. The value  $T_c = 11$  K obtained for Al-Si alloys with f.c.c. structure exceeds the superconducting characteristics of all non-transition metal alloys studied earlier.

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#### References

- /1/ M. HANSEN and K. ANDERKO, Constitution of Binary Alloys, McGraw-Hill Publ. Co., Inc., New York/Toronto/London 1958.
- /2/ W.B. PEARSON, The Crystal Chemistry and Physics of Metals and Alloys, Wiley Interscience, Inc., New York/London/Sydney/Toronto 1972.

- /3/ S.M. BANOVA, I.A. KORSUNSKAYA, G.M. KUSNEZOV, and V.A. SERGEEV, *Fiz. Metallov i Metallovedenie* 46, 521 (1978).
- /4/ B. PREDEL and G. SCHLUCKEBIER, *Z. Metallk.* 63, 198 (1972).
- /5/ H. MIJ, M. SENOO, and I. FUJISHIRO, *Japan. J. appl. Phys.* 15, 777 (1976).
- /6/ M. ITAGAKI, B.C. GIESSEN, and N.J. GRANT, *Trans. ASM* 61, 330 (1968).
- /7/ V.F. DEGTYAREVA, S.A. IVANENKO, E.G. PONYATOVSKII, and V.I. RASHUPKIN, *Fiz. tverd. Tela* 20, 412 (1978).
- /8/ V.F. DEGTYAREVA, G.V. CHIPENKO, E.G. PONYATOVSKII, and V.I. RASHUPKIN, *Fiz. tverd. Tela* 26, 1208 (1984).
- /9/ W.B. PEARSON, *Handbook Lattice Spacings and Structures of Metals and Alloys*, Vol. 2, Pergamon Press, 1967.
- /10/ A.K. MC MAHAN, M.T. YIN, and M.L. COHEN, *Phys. Rev. B* 24, 7210 (1981).
- /11/ V.F. DEGTYAREVA and E.G. PONYATOVSKII, *Fiz. tverd. Tela* 24, 2672 (1982).

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