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LATTICE PARAMETER AND DENSITY IN THE Ge-Si ALLOY SYSTEM*

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ABSTRACT

The lattice parameter and density of chemically analyzed samples of homogeneous Ge-Si alloy have been measured throughout the entire alloy system. The temperature dependence of the lattice parameter was measured between 25-800°C. Compositional dependences of the lattice parameter and density are accurate to about ± 0.3 atomic per cent in alloy composition. Lack of chemical analysis or sample inhomogeneity may explain the large discrepancies between previous investigations of these properties. The excess volume of mixing is given by $\Delta V_m^{xs} = -0.24 c_{Ge} c_{Si} \text{ cm}^3 \text{ mole}^{-1}$. Deviations from Vegard's law are negative as predicted by models based on first order elasticity theory, but smaller in absolute magnitude. This discrepancy is about the size of the positive deviations calculated from second order elasticity theory.

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INTRODUCTION

Composition in the Ge-Si alloy system can be accurately determined from measurements either of density or of lattice parameter provided the dependences of lattice parameter and density on composition are known. However, the large discrepancy between the results of previous investigations^(Table I) of these properties,¹⁻⁵ corresponds to an uncertainty in composition for a definite value of lattice parameter or density of $\pm 4\text{at}\% \text{Ge}$ throughout most of the system. This discrepancy can be attributed to the fact that no previous investigator has both evaluated sample homogeneity and determined composition by chemical analysis. Therefore the variation of lattice parameter and density at room temperature has been reinvestigated throughout the Ge-Si alloy system, using chemically homogeneous specimens. The temperature dependence of lattice parameter has also been measured in the range $25\text{-}800^\circ\text{C}$ for several alloy compositions.

EXPERIMENTAL PROCEDURE

Homogeneous Ge-Si alloy ingots were prepared from high purity Ge and Si by zone leveling using the procedure described by Dismukes and Ekstrom.⁶ Typical mass spectrographic analyses of impurities in these materials are shown in Table II. The procedure for this study consisted of first measuring the density

and then either measuring the lattice parameter or the chemical composition of the material⁷.

Densities were measured by the method of hydrostatic weighing,⁸ employing Archimedes' principle. The samples in the form of slices weighed 0.7-1.5 gm, and the weight loss in water was 0.1-0.3 gm. The samples were suspended from a 0.003 inch diameter tungsten wire, and were weighed to a precision of 0.02 mgm using a semimicrobalance. Water, to which a small amount of wetting agent had been added to reduce the surface tension, was used as the immersion liquid. The measurements were corrected for water temperature and for the air displaced by the sample, but not for effects due to the wetting agent, dissolved air, or atmospheric pressure. The absolute accuracy of these density measurements is shown to be within $\pm 0.1\%$ by comparison in Table III of measurements made on Si and Ge corrected to 25°C with the values of Smakula and Sils.⁸

Samples for lattice parameter measurements were ground to pass through a 325 mesh screen. The sieved powder was mixed with Duco cement and was then rolled into a fiber approximately 0.1 mm in diameter. The fiber was mounted in a 114.6 mm diameter camera using the asymmetric method of mounting the film. Powder patterns were obtained using Ni filtered Cu radiation, with an exposure time of about 24 hours and at room temperature of 25° \pm 1°C. The back reflection

lines, both $K\alpha_1$ and $K\alpha_2$, were measured to within $\pm 0.05\text{mm}$. The lattice parameter for each reflection was calculated, and the final value was obtained by extrapolation using the Nelson-Riley function. The absolute accuracy of the lattice parameter measurements is shown to be within $\pm 0.0005\text{\AA}$ by comparison in Table III of measurements made on Si and Ge with the values of Smakula and Kalnajs.⁹ The variation of lattice parameter with temperature in the range 25-800°C was determined by scanning the (531) and (620) diffraction peaks with a diffractometer. Values of the lattice parameter at each temperature were obtained by averaging the lattice parameter values for the two peaks. Good agreement between the diffractometer method and the Debye-Scherrer method was obtained at room temperature.

Chemical composition was determined by analyzing the material for its Ge content by the method of Cheng and Goydich⁷ using samples containing 150-300 mgn of Ge.

RESULTS

Data on measurements of density and lattice parameter at 25°C for different alloy compositions are listed in Table III. The variation of lattice parameter with density is shown in Fig. 1, and this is compared with published data. The curve is drawn through the data from the present study.

The scatter in the data of Johnson and Christian² and of Busch and Vogt,⁴ and the large systematic error in the latter

data, may be due to sample inhomogeneity. The preparative procedure employed by Johnson and Christian, slow cooling from the melt, could lead to this condition, since the growth rate was not controlled and the melt composition changed during growth. The growth rates employed by Busch and Vogt⁴ appear to have been too large for preparing homogeneous material by zone leveling in the middle of the system,⁶ where the discrepancy is greatest. There is good agreement between our results and the data of Wang and Alexander,³ who have shown that their material was homogeneous.

The curve for the variation of density with chemical composition, shown in Fig. 2, was drawn through the points determined by chemical analysis. Uncertainty in the recovery factor for Ge, $\pm 0.3\%$, is probably the largest source of error in the analysis.⁷ This effect contributes to the relatively large scatter at the Ge-rich end of the system. We also calculated from the curve in Fig. 1 the average atomic weight, \bar{A} , using the relation,

$$\bar{A} = d a^3 N/8 \quad (1)$$

where N is Avagadro's number,¹⁰ and from this the alloy composition. Points for density versus composition determined in this manner are also shown in Fig. 2.

The variation of lattice parameter with composition is shown in Fig. 3. The chemical composition was determined by (a) combining Figs. 1 and 2, and (b) using Eq. 1. The results

of Johnson and Christian² (Fig. 3) show some scatter, which could be due to sample inhomogeneity as discussed above, or to error in the polarographic analytical method as was pointed out by Cheng and Goydish.⁷ The results of Stohr and Klemm¹ are in better agreement with our data, but they show a large deviation at low Ge concentration. The values of Wang and Alexander³ show a large disagreement when plotted against the given compositions. This suggests that their specimens, though chemically homogeneous, differed in composition from the intended values by an average of about 7at%Ge. The lattice parameter data of Busch and Vogt⁵ was not compared with the results of the present work, because of both the lack of chemical analysis and of the large deviation observed in Fig. 1.

In Table IV are listed values of density and lattice parameter at 25°C for composition intervals of 5at%Ge. These values are derived from Figs. 1-3, and their absolute accuracy is probably within $\pm 0.3\text{at}\% \text{Ge}$. Values of density were taken as the mean of those from the curve in Fig. 2 and of those calculated from Eq. (1). The departure in lattice parameter from Vegard's law, Δ , given by,

$$\Delta = a_{\text{Ge-Si}} - \left\{ a_{\text{Si}} + (a_{\text{Ge}} - a_{\text{Si}}) c_{\text{Ge}} \right\}, \quad (2)$$

where c_{Ge} = atomic fraction Ge, is also listed in Table IV. This quantity is negative throughout the system and reaches a broad minimum in the middle of the system.

The excess volume of mixing, ΔV_m^{XS} , calculated using the

expression,

$$\Delta V_m^{XS} = \frac{N}{8} \left[a_{Ge-Si}^3 - \left\{ a_{Si}^3 + (a_{Ge}^3 - a_{Si}^3) c_{Ge} \right\} \right], \quad (3)$$

is also small and negative throughout the alloy system. From the plot of $\Delta V_m^{XS} / (c_{Ge} \cdot c_{Si})$ against c_{Ge} given in Fig. 4 it is seen that ΔV_m^{XS} can be expressed by the empirical relation,

$$\Delta V_m^{XS} = - 0.24 c_{Ge} \cdot c_{Si} \text{ cm}^3 \text{ mole}^{-1}, \quad (4)$$

where c_{Si} is the atomic fraction of Si.

The temperature dependence of the lattice parameter of Ge, Si, and three Ge-Si alloys is shown in Fig. 5 together with the average values of the linear expansion coefficient, $\bar{\alpha}$, between 25°C and 800°C. For Ge and the Ge-Si alloys, α is independent of temperature, but the data for Si indicates an increase in α of about 50% from 25°C to 800°C. A larger increase in α with temperature has been reported by Dutta.¹³ For the alloys containing 20.1at%Ge and 34.7at%Ge, the deviation from Vegard's law and the excess volume of mixing are constant with temperature within the experimental uncertainty of about $\pm 15\%$ of these quantities. In the 51.7at%Ge alloy, these deviations decrease about 25% between 25°C and 800°C.

DISCUSSION

Volume of Mixing

The observation that ΔV_m^{XS} can be expressed by equation (4) suggests that the Ge-Si alloy system might show a simple type of

thermodynamic behavior.¹⁴ Since ΔV_m^{XS} is not zero, the system is not an ideal solution, in agreement with Thurmond's¹⁵ conclusion from the nature of the phase diagram. The next simplest type of behavior is regular solution theory in which $\Delta S_m^{XS} = 0$. The quasichemical approach to regular solution theory¹⁶ leads to the expression,

$$\Delta H_m^{XS} = -\Omega c_{Ge} c_{Si}, \quad (5)$$

where Ω is related to the bond energies H_{Ge-Ge} , H_{Si-Si} , and H_{Ge-Si} by,

$$-\Omega = 4 \left[H_{Ge-Si} - \frac{1}{2} \{ H_{Ge-Ge} + H_{Si-Si} \} \right]. \quad (6)$$

From quasichemical theory one would expect that Ω and ΔV_m^{XS} have the same sign. Rastogi and Nigam¹⁷ have calculated a value of $+20 \text{ kcal mole}^{-1}$ for Ω from a quasichemical regular solution treatment of the Ge-Si alloy phase diagram. We have repeated their calculation considering a larger section of the phase diagram, and obtain the value $+2.4 \text{ kcal mole}^{-1}$. Thus while the value of Ω is quite uncertain, the sign is probably correct. Since Ω and ΔV_m^{XS} are not of the same sign, a more refined model will be required to explain the thermodynamic properties of the Ge-Si alloy system.

Deviations from Vegard's Law

The Ge-Si alloy system is an attractive one for comparing experimental deviations from Vegard's law with theoretical calculations, since there is only one crystal structure in the

system, no relative valency effect, and only small differences in size and electronegativity between the constituents. A summary of the theoretical work on this topic was recently given by Gschneidner and Vineyard.¹⁸ The deviations from Vegard's law predicted by theories which require data only on the elastic properties of the pure components are shown in Fig. 6. Pines¹⁹ used an elastic sphere model to derive the equation,

$$\Delta = c_A c_B (a_B - a_A) \left[\frac{4/3 \mu_A (\chi_A - \chi_B)}{1 + 4/3 \mu_A (c_B \chi_A + c_A \chi_B)} \right], \quad (7)$$

where A refers to the solvent, B to the solute, μ is the shear modulus, and χ is the compressibility. Fournet²⁰ considered the effects of nearest neighbor interactions to obtain the equation,

$$\Delta = c_A c_B (a_B - a_A) \left[\frac{(\chi_A/\chi_B) - 1}{c_A + c_B (\chi_A/\chi_B)} \right]. \quad (8)$$

Both equations (7) and (8) predict negative deviations when the element with the larger atom is softer. Thus they give the correct sign of the deviation for the Ge-Si alloy system, but the predicted magnitude is about twice the experimental value.

Friedel²¹ treated the elastic sphere model so as to obtain the equation,

$$\Delta = c_B(a_B - a_A) \left\{ \left(\frac{\chi_A}{\chi_B} \right) - 1 \right\} \left/ \left[\left\{ \frac{(1 + \sigma_A)\chi_A}{2(1 - 2\sigma_A)\chi_B} \right\} + 1 \right] \right. , \quad (9)$$

where σ_A is Poisson's ratio. This equation is valid only for dilute solutions, but within this limit it is in better agreement with experiment than those of Pines¹⁹ and Fournet.²⁰

Gschneidner and Vineyard¹⁷ applied second order elasticity theory to obtain the equation,

$$\Delta = 2 \left(\frac{d\mu}{dp} - \frac{\mu}{B} \right) \frac{(a_A - a_B)^2}{a_A} c_B , \quad (10)$$

where p is pressure and B is the bulk modulus. This equation is also valid only for dilute solutions. They suggest the approximation,

$$\left(\frac{d\mu}{dp} - \frac{\mu}{B} \right) \approx 6\alpha V\mu/c_V , \quad (11)$$

where V is the molar volume and c_V is the molar heat capacity. This equation predicts only positive deviations from Vegard's law. However, the magnitude of its effect is comparable to the amount by which the first order theories overestimate the negative deviations. This suggests that a theory combining both first and second order elasticity effects would be a considerable improvement over current theories for predicting deviations from Vegard's law.

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TABLE I

Authors	Method of Preparation	Lattice Parameter	Density	Method of Analysis
Stöhr and Klemm ¹	Sintering	D	ND	None ^a
Johnson and Christian ²	Slow Cooling from the Melt	D	D	Polarographic
Wang and Alexander ³	Zone Leveling	D	D	None ^b
Busch and Vogt ⁴	Zone Leveling	D	D	None ^c
Sandulova, et al. ⁵	Vapor Transport	D	ND	None ^d

D = Determined

ND = Not Determined

a = Composition assumed to be that of the mixed components before sintering.

b = Composition assumed to be that of the mixed components before zone leveling.

c = Composition determined from the results of Johnson and Christian.

d = Composition assumed to be that of the mixed components before vapor transport.

TABLE II

Materials	TYPICAL IMPURITY CONTENTS, Atomic ppm						
	Fe	Cu	Al	Mg	O	C	H
Ge -Si	1	.2	5	1	300	30	100
Ge	6	ND	.4	.4	10	100	30
Si	1	.2	1	1	300	100	10

ND = Not detected

TABLE III

d (gm cm ⁻³)	a (Å)	C (at.% Ge)
2.6382	---	7.5
2.6319	---	8.0
2.6357	---	8.0
2.6330	5.4492	8.4 # 1
3.0047	---	18.9
3.0098	---	20.0
3.0710	---	21.4
3.0830	---	21.7
3.0120	5.4726	20.1 # 2
3.0822	5.4772	22.3 # 3
3.0884	---	22.6
3.1118	---	23.5
3.2723	---	28.2
3.2844	5.4898	28.7 # 4
3.3634	---	30.5
3.3585	---	31.6
3.4735	5.5032	31.8 # 5
3.4762	---	35.4
3.5181	---	35.5
3.5715	---	36.6
3.6312	5.5151	39.7 # 6
3.6313	---	38.8
3.6340	---	39.8
3.6874	---	40.3
3.6766	---	41.4
3.7750	5.5250	44.3 # 7
3.7827	---	44.5
3.7883	---	44.6
3.9915	5.5404	51.4 # 8

TABLE III (Cont.)

<u>d (gm cm⁻³)</u>	<u>a (Å)</u>	<u>C (at.% Ge)</u>
3.8944	---	48.0
3.9940	---	49.9
4.0037	---	50.6
4.0749	5.5475	54.0 #9
4.0673	---	53.8
4.0897	---	54.8
4.1652	---	57.0
4.1923	5.5567	58.0 #10
4.5289	5.5841	69.6 #11
4.5170	---	68.0
4.4969	---	68.9
4.6817	5.5966	75.0 #12
4.6652	---	71.9
4.6735	---	72.3
4.8246	---	79.4
4.8513	---	79.4
4.8410	5.6112	80.9 #13
5.0752	5.6325	89.9 #14
5.0754	---	87.3
5.0728	---	87.9
5.0970	---	88.8
5.0410	---	89.4
5.1090	---	90.8
5.1697	5.6419	93.7 #15
5.1669	---	94.8
5.3256	5.6575	Ge ^a
5.32674	5.65754	Ge ^b
2.3277	5.4310	Si ^a
2.32902	5.43072	Si ^b

a Present work

b Smakula and Sils⁹ and Smakula and Kalnajs¹⁰

TABLE IV

<u>C (at % Ge)</u>	<u>d (gm cm⁻³)</u>	<u>a (Å)</u>	<u>a - a_v (Å)</u>
0	2.3277	5.4310	---
5	2.5100	5.4419	-.0004
10	2.6825	5.4522	-.0014
15	2.8490	5.4624	-.0026
20	3.0075	5.4722	-.0041
25	3.1660	5.4825	-.0051
30	3.3265	5.4928	-.0062
35	3.4840	5.5038	-.0065
40	3.6405	5.5149	-.0067
45	3.7950	5.5261	-.0068
50	3.9470	5.5373	-.0069
55	4.0990	5.5492	-.0063
60	4.2465	5.5609	-.0060
65	4.3905	5.5727	-.0055
70	4.5335	5.5842	-.0053
75	4.6730	5.5960	-.0048
80	4.8115	5.6085	-.0027
85	4.9445	5.6206	-.0019
90	5.0740	5.6325	-.0023
95	5.1990	5.6448	-.0013
100	5.3256	5.6575	----

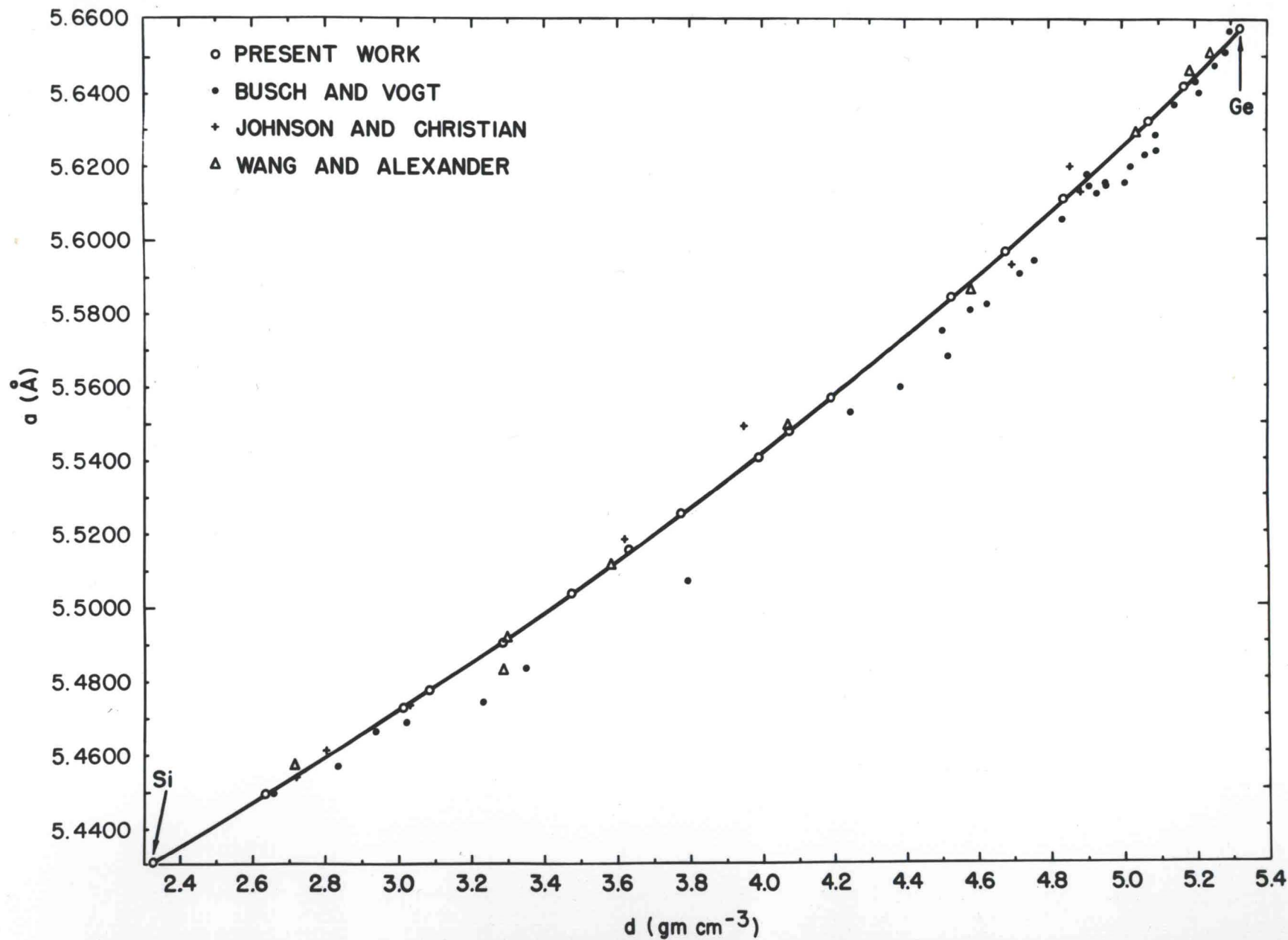


FIG. 1

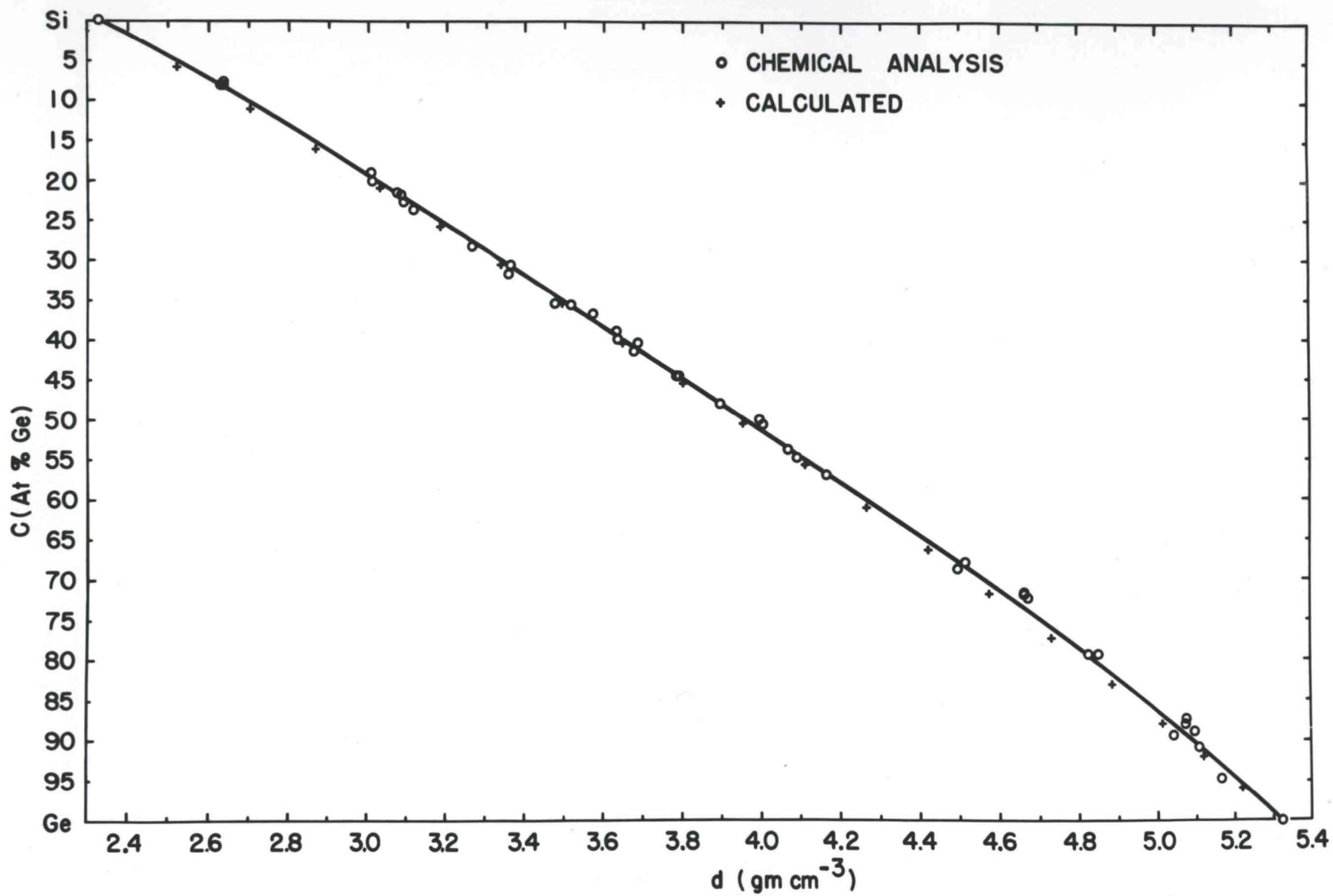
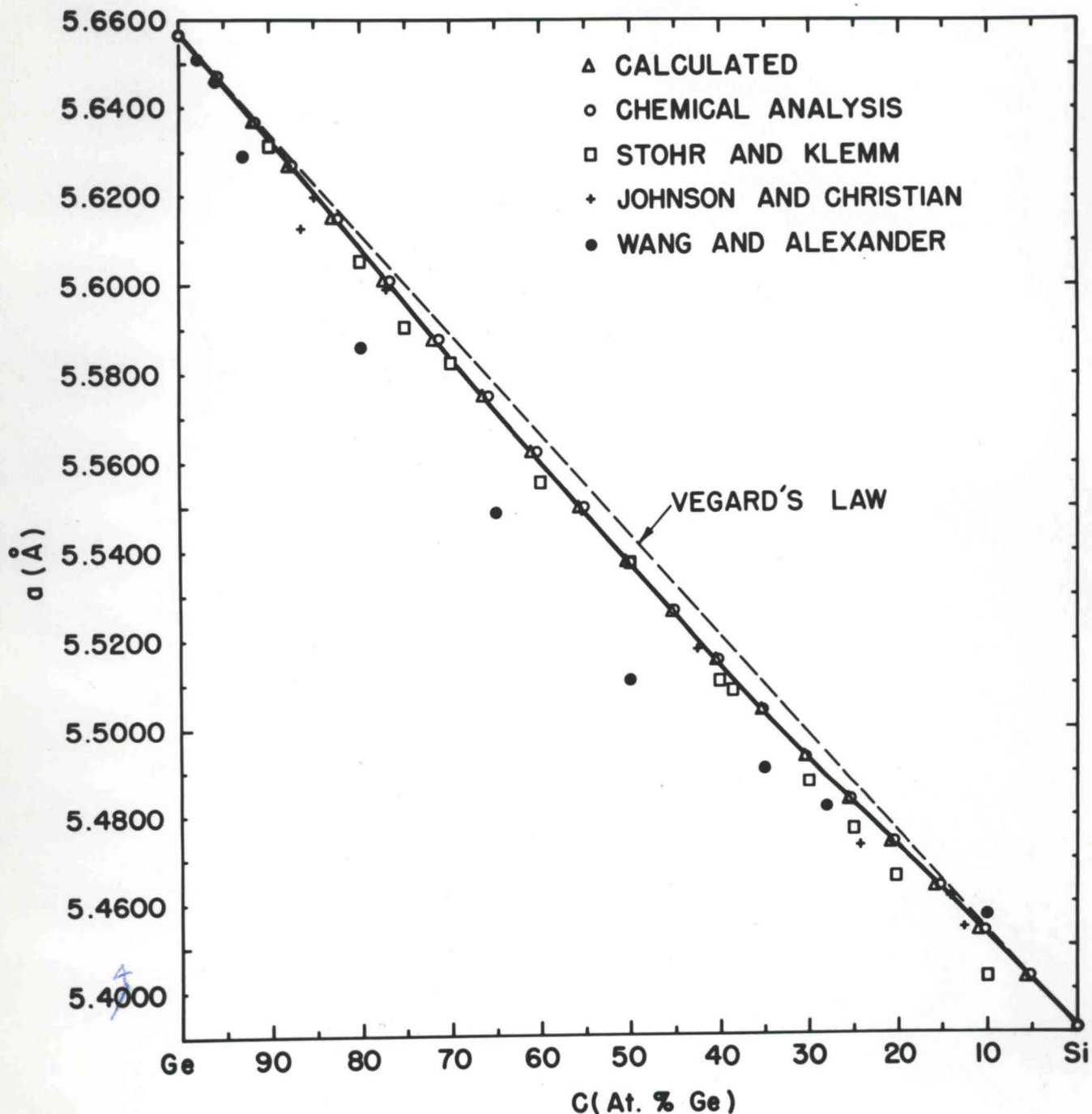


Fig. 2



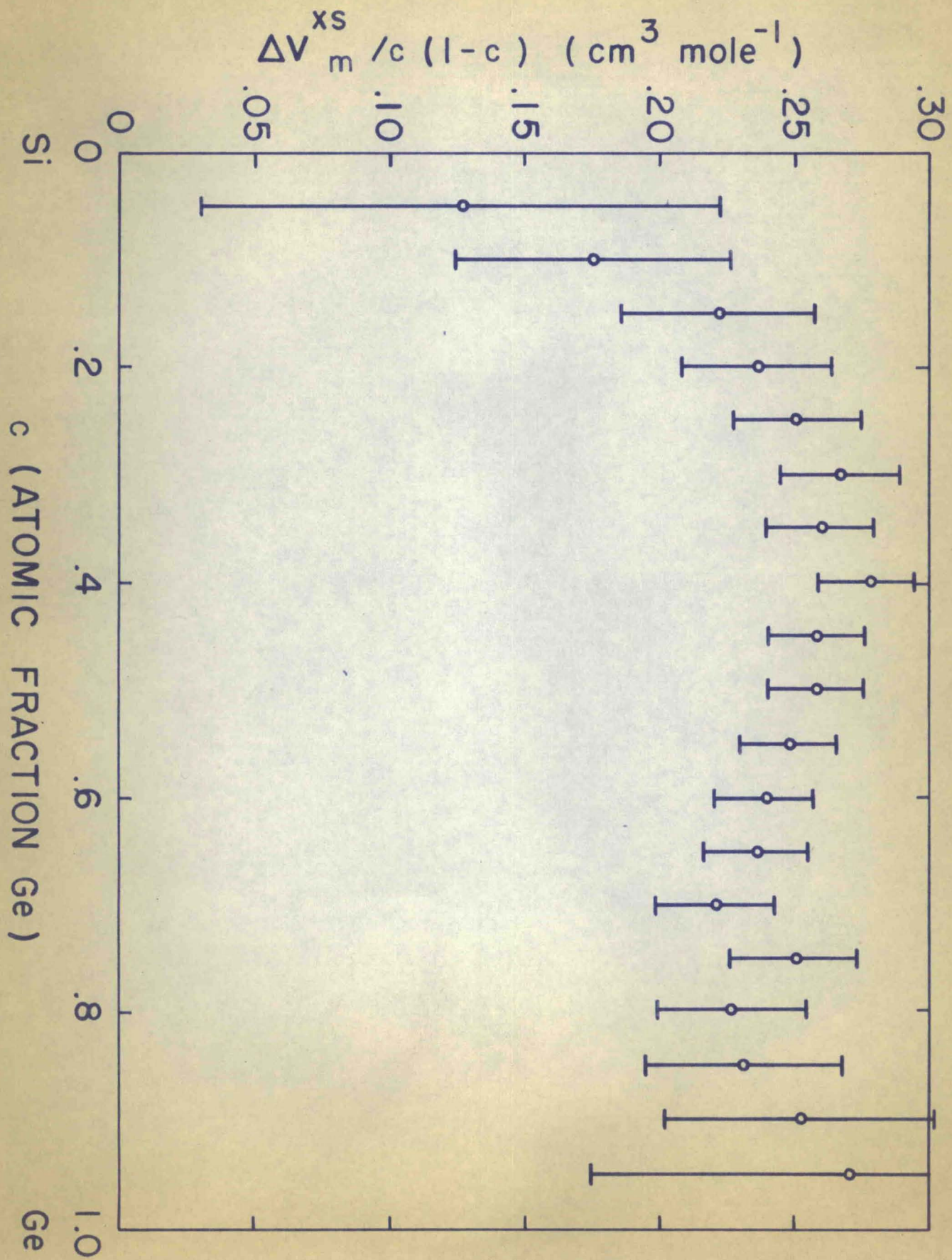
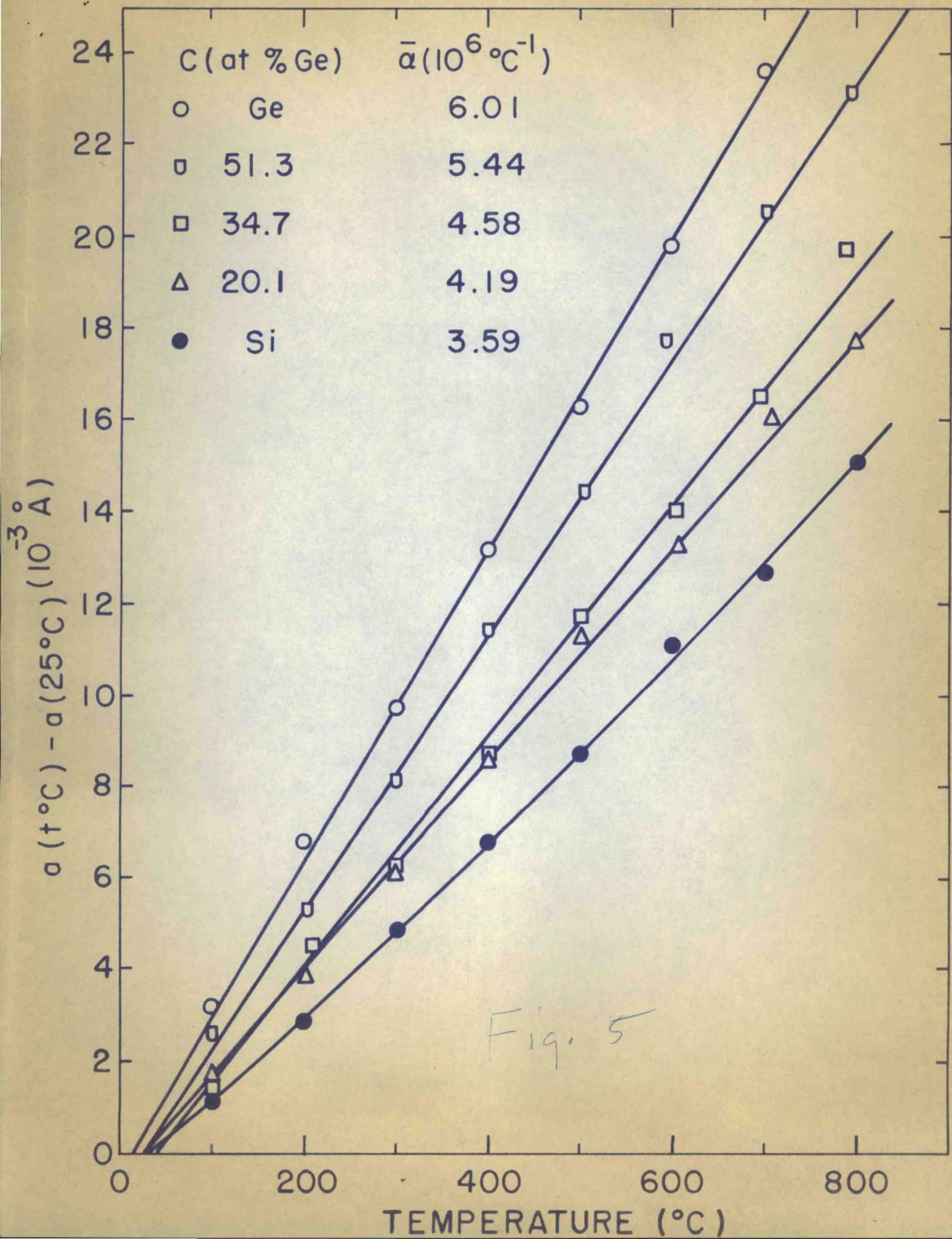


Fig. 19.4



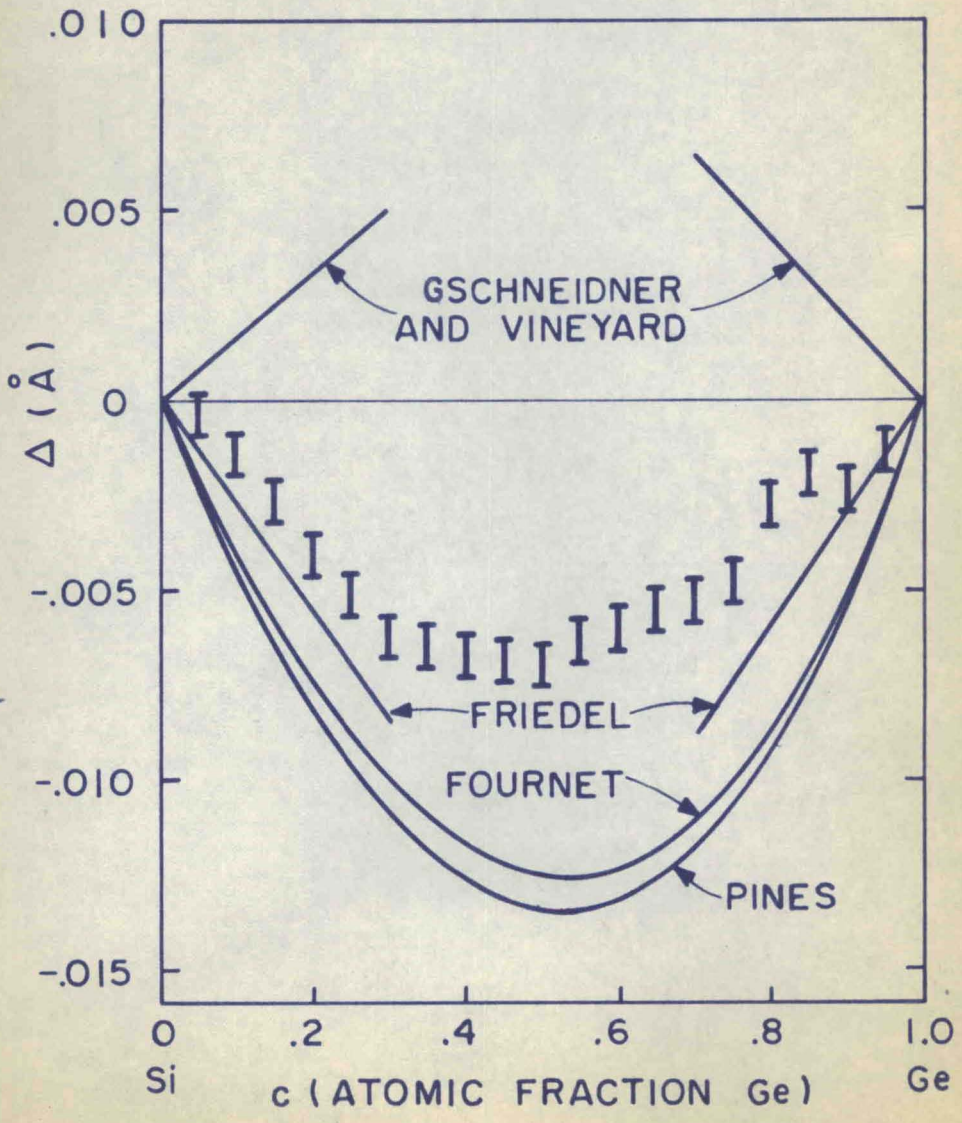


Fig 6