Greek Letters

ψ = potential energy between two molecules, ergs
ϵ = minimum potential energy between two molecules, ergs
σ = distance of separation of two molecules in the Lennard-Jones potential when the potential energy equals zero, A.
μ = dipole moment of polar molecule, debyes
ρ_0 = distance between molecules in the Kihara potential when the potential energy is a minimum, A.
ρ = distance between molecules in the Kihara potential, A.
α = polarizability, $cm.^3$
ξ = correction factor for dipole-induced interaction
θ_1,θ_2 = angles made by two molecules in relation to line joining their centers
ϕ_2-ϕ_1 = angle between the planes which pass through the line of their centers and contain the two axes of the two molecules

Subscripts and Superscripts

11 = nonpolar component
22 = polar component
12 = interaction parameter for polar and nonpolar component
M = mixture parameter
np = nonpolar contribution of parameter in polar component
s = Stockmayer parameter
$'$ = parameter corrected for dipole-induced dipole interaction

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Lattice Parameter and Density in Bismuth-Antimony Alloys

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The hexagonal lattice parameters (a and c) and density (d) of chemically analyzed samples of homogeneous Bi-Sb alloy have been measured at 25° C. throughout the entire alloy system. Compositional dependences of a and c and d have an absolute accuracy of ±0.3 atomic % Sb. The excess volume of mixing, ΔV_m^{xs}, is close to zero in this system, indicating ideal thermodynamic behavior. Thus, it would be interesting to investigate ΔH_m^{xs} and ΔS_m^{xs} to determine whether the system is truly ideal.

In recent years, there has been considerable interest in the electrical, thermal, and thermomagnetic properties of Bi-Sb alloys (*4, 12, 13, 16, 19*). The older investigations of the dependence of lattice parameter upon alloy composition in this system were either of insufficient accuracy (*2, 11*) or were made (*12*) on specimens not prepared under conditions of slow growth which were necessary to obtain homogeneous material (*3, 14, 20*). More recent measurements of lattice parameter on homogeneous specimens have been limited to Bi-rich alloys (*7, 10*). No measurements of the dependence of density upon alloy composition in the Bi-Sb alloy system have been reported. The purpose of this work is to establish accurately the dependences, respectively, of lattice parameter and density upon composition throughout the entire Bi-Sb alloy system.

EXPERIMENTAL PROCEDURES AND RESULTS

Homogeneous Bi-Sb alloy ingots were prepared from high-purity Bi and Sb by zone leveling using the procedure described by Yim and Dismukes (*20*). Typical mass spectrographic analyses of impurities in these materials are shown in Table I. The procedure for this study consisted of first

Table I. Mass Spectrographic Analysis of Starting Materials and Homogeneous Bi-Sb Alloys

Impurity Elements[a] Atomic, P.P.M.	Starting Materials		Homogeneous Alloys			
	Bi	Sb	$Bi_{95}Sb_5$	$Bi_{88}Sb_{12}$	$Bi_{50}Sb_{50}$	$Bi_{10}Sb_{90}$
Mg	0.3	0.6	0.2	2.1	0.2	0.3
Al	0.2	0.3	0.3	0.1	0.3	...
Si	1.0	2.4	3.9	1.4	5.4	5.4
Ca	0.4	0.7	0.4	0.1	0.6	...
Cr	0.1	0.7	0.4	0.5	...	0.6
Fe	0.5	2.1	0.9	0.9	1.0	1.0
Cu	0.5	0.2	0.3	0.1	0.3	...
Zn	1.9	0.3	...	0.8	...	...
Ga	0.5	...	...	...	0.2	0.9
As	0.1	2.7	...	...	1.1	3.0
Ag	0.2	...	0.8	...	...	0.1
Sn	...	0.1	...	...	...	0.5
Pb	0.1	0.6	...	...	0.3	0.4
Sb	6.0	MC	MC	MC	MC	MC
Bi	MC[b]	...	MC	MC	MC	MC

[a] Metallic impurities only. [b] Major components.

measuring the density and then measuring the lattice parameter or the chemical composition of the material.

Density. Densities were measured by the method of hydrostatic weighing (*9*), employing Archimedes' principle. The samples, in the form of slices, weighed 1.5 to 3 grams, and the weight loss in water was 0.1 to 0.3 gram. The samples were suspended from a 0.002-inch diameter platinum wire and were weighed to a precision of 0.01 mg. using a microbalance. Water at 25 ± 1° C., to which a small amount of wetting agent had been added to reduce the surface tension, was used as the immersion liquid. The density of the water was determined from the apparent density of Ge, taking the density (*15*) of Ge as 5.32674 grams $cm.^{-3}$ at 25° C.

Data on the measurements of density at 25° C. are listed in Table II for different alloy compositions. The value of density obtained for antimony, 6.6892 grams $cm.^{-3}$, is slightly lower than the value 6.6973 grams $cm.^{-3}$ obtained by Cahill and Kirshenbaum (*5*), but is in good agreement with the x-ray density calculated from the present authors' lattice parameter data, 6.6922 grams $cm.^{-3}$. The value of the density obtained for bismuth, 9.8047 grams $cm.^{-3}$, is in good agreement both with the literature value (*21*) and the x-ray density calculated from our lattice parameter data, 9.8044 grams $cm.^{-3}$.

Table II. Experimental Values of Density, *d*, Lattice Parameters, *a* and *c*, and Chemical Composition, C, for Bi-Sb Alloy Samples at 25° C.

d, G. $Cm.^{-3}$	*a*, *A.*	*c*, *A.*	*C*, Atomic % Sb
9.8047	...	...	0
9.8047	4.5465	11.8616	0
9.7586	...	...	2.03
9.7632	4.5424	11.8529	...
9.7583	...	...	1.13
			3.16
9.6861	...	...	3.19
			4.71
9.6800	...	...	4.91
9.6805	4.5355	11.8383	...
9.6237	...	...	6.42
9.6133	...	...	7.20
9.6199	4.5294	11.8257	...
9.5379	...	...	9.80
9.5273	...	...	9.88
9.5347	4.5242	11.8151	...
9.4409	...	...	13.18
9.4359	...	...	13.10
9.4446	4.5150	11.7963	...
9.3552	...	...	15.60
9.3445	4.5064	11.7777	...
9.1691	4.4923	11.7486	...
9.3321	...	...	16.10
9.2739	...	...	18.20
9.1879	...	...	20.0
9.1756	...	...	20.4
			22.0
8.8581	...	...	31.9
8.8615	4.4655	11.6936	
8.7702	4.4575	11.6796	...
8.8677	...	...	34.20
			34.0
8.7842	...	...	35.7
			37.4
8.3122	...	...	48.7
8.3088	4.4227	11.6031	...
8.3097	...	...	50.5
			50.8
7.5861	...	...	72.5
7.5873	...	...	72.5
7.5850	4.3590	11.4413	...
7.5883	4.3685	11.4670	...
7.0919	...	...	88.2
7.4016	4.3564	11.4354	...
7.0914	...	...	88.7
7.0920	4.3366	11.3719	...
6.6892	4.3085	11.2732	100
6.6892	...	...	100

Lattice Constant Determination. The unit cell parameters for Bi, Sb, and selected Bi-Sb alloy compositions were determined to an average absolute accuracy of better than 1 part in 10,000 using the Debye-Scherer x-ray powder method. Computer methods were employed extensively in the determinations and proved to be a valuable asset.

The samples in the form of slices were ground to pass 400-mesh screens, annealed at 200° C. for 16 hours to remove strain, and were loaded into thin-walled, low-absorbing glass capillaries 0.2 mm. in diameter. All powder patterns were

Table III. Interplanar Spacings and Intensity Measurements of Hexagonal Bi and Sb at 25° C.

Antimony			Bismuth		
hkl	*d*, A.	*I*	*hkl*	*d*, A.	*I*
003	3.735	W	003	3.939	VW
101	3.520	VW	101	3.727	VVW
102	3.095	VS	102	3.271	VS
104	2.242	VS	104	2.364	S
110	2.148	VS	110	2.268	S
105	1.926	M	105	2.029	W
006	1.872	M	006,113	1.971	W
202	1.768	S	202	1.867	M
204	1.553	M	204	1.639	M
107	1.477	M	107	1.554	W
205	1.436	W	205	1.513	VW
116	1.414	M	116	1.490	M
212	1.367	M	212	1.443	M
108	1.318	W	108	1.387	W
214	1.2605	M	214	1.3296	M
009	1.2517	W	009	1.3186	M
300	1.2430	M	300	1.3123	W
207	1.2191	W	207	1.2834	W
215	1.1955	W	215	1.2611	VW
303	1.1804	VW	303	1.2450	VVW
208	1.1234	W	208	1.1848	VW
119	1.0823	M	119	1.1402	W
220	1.0763	M	220	1.1366	W
217	1.0605	M	217	1.1176	VW
306	1.0364	M	306	1.0927	W
312	1.0174	M	312	1.0735	W
218	0.99676	M	218	1.0500	W
10.11	0.98810	M	10.11	1.0395	W
314	0.97124	M	314	1.0242	W
20.10	0.96463	VW	20.10	1.0160	VW
315	0.94051	W	315	0.99164	VW
226	0.93424	M	226	0.98503	W
402	0.91996	M	402	0.97048	W
20.11	0.89802	M	20.11	0.94553	VW
404	0.88516	M	404	0.93422	VW
309	0.88233	M	309	0.92999	VW
21.10	0.88019	M	21.10	0.92757	W
317	0.87046	W	317	0.91793	W
405	0.86150	VW	405	0.90919	VVW
322	0.84605	M	322	0.89277	W
10.13	0.84421	M	10.13	0.88870	W
318	0.83405	W	318	0.87912	W
21.11	0.82886	M	21.11	0.87309	W
324	0.81887	M	324	0.86398	W
410	0.81404	M	410	0.85916	M
407	0.80712	VW	407	0.85131	VW
325	0.80016	W	325	0.84417	VW
413	0.79567	W	413	0.83960	VW
20.13	0.78638	M	20.13	0.82775	W
408	0.77779	W	408	0.81995	W
			31.10	0.80329	VW
			327	0.79704	W
			00.15	0.79085	VW
			416	0.78798	M
			502	0.78058	W
			21.13	0.77787	M

obtained at 25° ± 1° C. on 114.6-mm. diameter powder cameras with nickel filtered copper radiation. The asymmetric (Straumanis) method of film mounting was used, and the diffraction lines were read with a millimeter scale and vernier to an accuracy of ±0.05 mm. Smooth, sharp, and well-resolved diffraction lines were obtained throughout the entire alloy system.

A search of the A.S.T.M. index file and other sources (*1*, *17*, *18*,) indicated that the patterns listed for pure Sb and Bi were not completely indexed for CuKα radiation, particularly in the high angle region, where one obtains the greatest sensitivity and accuracy in lattice constant determination. To index these lines for Bi and for Sb, a method of successive approximation was used, by taking the lattice parameters calculated from the lower angle indexed lines of Bi and Sb, and generating all of the possible *h*, *k*, *l*, and "*d*" values on the computer. After eliminating reflections forbidden by space group considerations, the higher angle reflections were indexed. Then the final lattice parameters were determined from all nonoverlapping $K\alpha_1$ and $K\alpha_2$ reflections having 2θ values greater than 120°, using the least squares method of Cohen (*8*). Conversion to a rhombohedral unit cell is an integral part of the computer program. The calculated rhombohedral parameters are: for Bi; a = 4.7459 A., α = 57.24°; and for Sb; a = 4.5065 A., α = 57.11°.

The observed indexed powder patterns for Sb and Bi are given in Table III. Reflections which were close enough to each other to cause line broadening and not be completely resolved as well as $K\alpha_2$ reflections, were omitted for the sake of simplicity.

Once the two end points, Bi and Sb, were characterized and indexed, their patterns were useful as visual standards for indexing the intermediate alloys. In the first step, only unambiguous reflections which had undergone a shift in 2θ angle were used to obtain unit cell parameters for the alloys. Then, using the same computer methods described for Bi and Sb, accurate unit cell parameters were determined.

The values of hexagonal lattice parameters (a and c) for Bi, Sb, and Bi-Sb alloys are listed in Table II. The values for Bi are in good agreement with those of Cucka and Barrett (*7*) and Swanson, Fuyat, and Ugrinic (*18*). The values of Sb are in good agreement with those of Barrett, Cucka, Haefner (*1*) and Swanson, Fuyat, and Ugrinic (*17*).

Chemical Analysis. Samples of Bi-Sb alloy were dissolved in nitric acid and analyzed for combined content of Bi and Sb and for Sb alone by the EDTA method developed by Cheng and Goydish (*6*) for (Bi, Sb_2)Te_3 alloys. The data for a series of samples covering the entire Bi-Sb alloy system are given in Table II.

DISCUSSION

The dependences of the lattice parameters, a and c, respectively, upon density d are shown in Figure 1. There is a positive deviation in a from Vegard's law (linear interpolation) and a negative deviation in c from Vegard's law.

The curve for the variation of density with chemical composition for Bi-Sb alloys (Figure 2) was drawn through the points determined by chemical analysis. The absolute accuracy of the curve is about ±0.3 atomic % Sb. The curve is in good agreement with the open circle data points calculated from Figure 1 in the following manner. From Figure 1 the average atomic weight, $\bar{A}$, was calculated from the relation,

$$\bar{A} = \frac{da^2cN[3]^{1/2}}{12} \qquad (1)$$

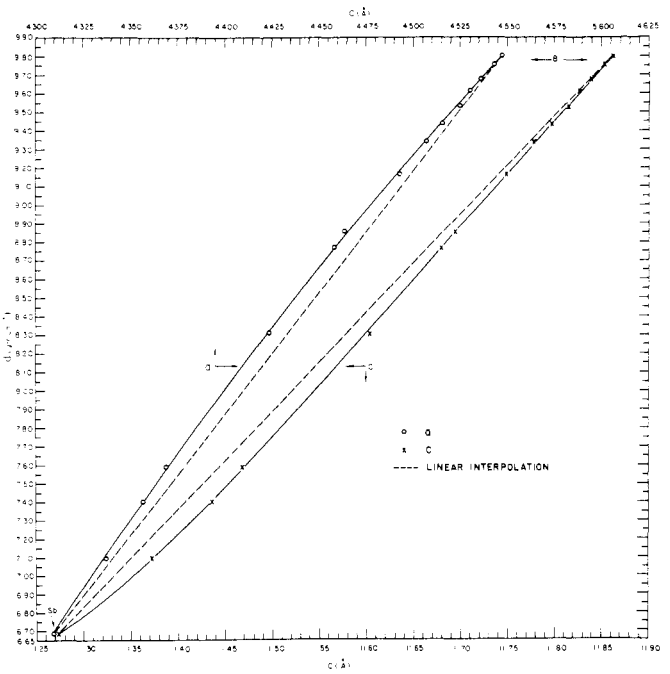

Figure 1. Variation of lattice parameters (a and c) with density (d) in the Bi-Sb alloy system at 25° C.

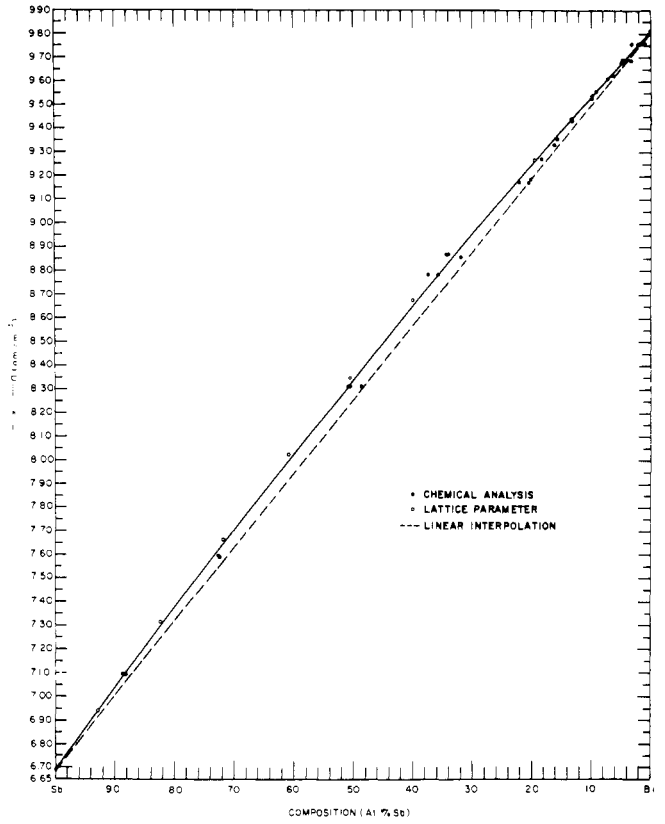

Figure 2. Variation of density (d) with chemical composition in the Bi-Sb alloy system at 25° C.

where N = 6.02311 × 10^{23} (mole)$^{-1}$ is Avogadro's number (*21*). From $\bar{A}$, one obtains the alloy composition.

The variation of the lattice parameters, c and a, with alloy composition is shown in Figure 3. There is good agreement between these data and those of Dugué (*10*) and of Cucka and Barret (*7*). The poor agreement with the data of Jain (*12*) is probably due to alloy inhomogeneity or lack of chemical analysis for his samples. There is a

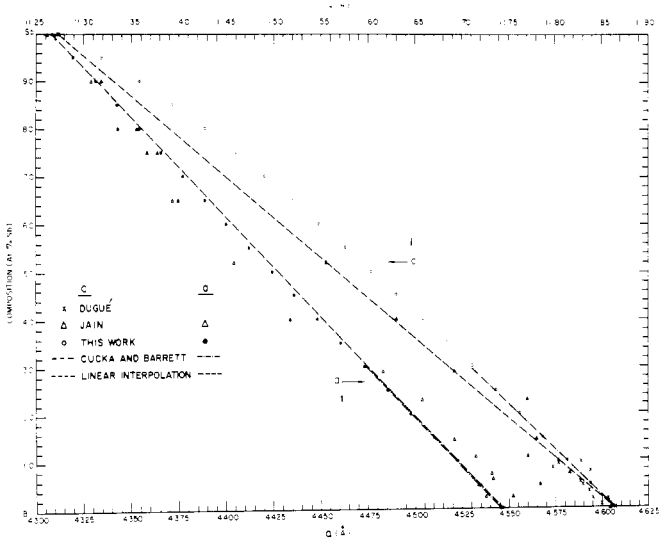

Figure 3. Variation of lattice parameters (a and c) with composition in the Bi-Sb alloy system at 25° C.

Table IV. Density and Lattice Parameters for Bi-Sb Alloy at 25° C. Derived from Figures 1 through 3

Composition, Atomic % Sb	d, G., Cm.$^{-3}$	a, A.	c, A.
100	6.6892	4.3085	11.2732
95	6.8630	4.3198	11.3195
90	7.0340	4.3313	11.3588
85	7.2025	4.3427	11.3945
80	7.3720	4.3542	11.4282
75	7.5370	4.3660	11.4605
70	7.6985	4.3772	11.4906
65	7.8600	4.3887	11.5200
60	8.0200	4.4000	11.5480
55	8.1780	4.4120	11.5760
50	8.3340	4.4242	11.6037
45	8.4920	4.4360	11.6310
40	8.6500	4.4483	11.6585
35	8.8025	4.4605	11.6846
30	8.9515	4.4730	11.7105
25	9.0970	4.4855	11.7360
20	9.2420	4.4978	11.7615
15	9.3860	4.5100	11.7867
10	9.5300	4.5225	11.8120
5	9.6700	4.5347	11.8365
0	9.8047	4.5465	11.8616

very small negative deviation in a from Vegard's law, and a somewhat larger positive deviation in c from Vegard's law. However, the combined effect leads to nearly ideal thermodynamic behavior of the volume of mixing. The excess volume of mixing, per mole, ΔV_m^{xs}, was calculated from the relation,

$$\Delta V_m^{xs} = \frac{[3]^{1/2}N}{12}[a_{Sb}^2 c_{Sb} + x(a_{Bi}^2 c_{Bi} - a_{Sb}^2 c_{Sb}) - a_{Bi-Sb}^2 c_{Bi-Sb}] \quad (2)$$

where x is the mole fraction of antimony. The values of reduced volume of mixing, $\Delta V_m^{xs}/(x)\ (1 - x)$, were about +0.051 cm.^{3} mole^{-1} for $0 < x < 0.65$ and about −0.008 cm.^{3} mole^{-1} for $0.65 > x > 1.0$. Since these values are more than one order of magnitude smaller than those found for Ge-Si alloys, apparently, within the accuracy of the measurements, ΔV_m^{xs} is zero and the behavior of volume ideal.

In Table IV are listed values of density (d) and hexagonal lattice parameters (a and c) at 25° C. for composition intervals of 5 atomic % Sb. These values are derived from Figures 1 through 3, and their absolute accuracy is within ±0.3 atomic % Sb.

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