

probably be used from $Z=53$ (I) till about $Z=66$ (Dy). Calculations have been undertaken in this laboratory and will be reported in due course.

2. Only planes with a high value of G_H should be plotted. Probably values larger than unity will be needed, but this point cannot be decided without further study.

3. Experimental errors in F_H should be kept as low as possible, for the reasons explained in the text. Visual estimates of intensities would probably be of little use when utilizing this technique.

4. As $f'(\lambda_1) - f'(\lambda_2)$ is nearly independent of $\sin \theta$, only one graph is necessary, except perhaps for crystals with rather high temperature factors.

5. The arguments can easily be extended to include the case where more than one kind of $A.S.$ is present in the structure.

Resumen

En este trabajo se propone un método para resolver estructuras centrosimétricas con dispersores anómalos

en forma análoga a la usada por Hargreaves en estructuras centrosimétricas a dispersión normal.

Se muestra que la diferencia entre los valores de un factor de estructura medidos con dos longitudes de onda diferentes ($F_H(\lambda_1)$ y $F_H(\lambda_2)$) es una magnitud compleja cuya fase es constante. Se obtiene así una relación lineal entre $F_H(\lambda_1)$ y $F_H(\lambda_2)$ y trazando un diagrama de correlación se puede fácilmente asignar los signos de las distintas reflexiones.

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The Crystal Structure of Bi and of Solid Solutions of Pb, Sn, Sb and Te in Bi

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Lattice constants, atomic positional parameters and Debye-Waller temperature factors were measured for Bi and Bi-rich binary solid solutions containing atomic percentages 0 to 30 Sb, 0-39 Pb, 0-125 Sn, 0-15 Te, and 0-22 Te at 4-2, 78, and 298 °K. The alloys were made by zone levelling and were based on very pure, zone refined Bi. The lattice constants of the Bi-Sb alloys vary linearly in the composition range $x=0$ to 30 atomic percent Sb. The variation can be described by the equations:

$$\begin{aligned} a &= 4.546 - 23.84 \cdot 10^{-4}x, \quad c = 11.863 - 51.66 \cdot 10^{-4}x, \quad \text{at } 298 \pm 3 \text{ }^\circ\text{K.}; \\ a &= 4.534 - 21.92 \cdot 10^{-4}x, \quad c = 11.814 - 48.75 \cdot 10^{-4}x, \quad \text{at } 78 \text{ }^\circ\text{K.}; \\ c &= 11.803 - 40.75 \cdot 10^{-4}x \text{ at } 4.2 \text{ }^\circ\text{K.} \quad (a, c \text{ in } \text{Å}); \end{aligned}$$

the average error is estimated to be 1 part in 2000. The atomic positional parameter z in the Bi-Sb alloys remains approximately constant up to about 12% Sb, and then rises from 0.23407 to 0.23420 at 4.2 °K., 0.23400 to 0.23413 at 78 °K., as the Sb content increases from 0 to 30 atomic percent Sb; the standard deviations of the z 's are estimated as 25×10^{-6} . At room temperature $z = 0.23389$. At 78 °K. the z for the other alloys is not significantly different from the value for pure Bi. The temperature factors B , for vibrations parallel to the c axis, are approximately 0.10, 0.32 and 1.14 at 4.2, 78 and 298 °K., respectively, for pure Bi, and increase slightly with increasing Sb content in the Bi-Sb alloys.

Introduction

Precision structure data on bismuth of extreme purity and its alloys are needed to guide the development of theories on the influence of band structure on crystal structure in these materials, such as the one proposed by Blount & Cohen (unpublished) referred to by Jain (1959) and Barrett (1960), in which it was postulated

that the distribution of electrons in conduction and valence bands directly controls the magnitude of the atomic parameter z , and that consequently z should be altered by changes in electron concentration and temperature. The determinations of the bismuth atomic parameter by James (1921), Hassel & Mark (1924), and Goetz & Hergenrother (1932) are inadequate for present needs; a determination was made

by Barrett (1960) in which both accuracy and sample purity were greatly increased. Further improvements in experimental and computational procedures were made in the present work and further attention was given to possible uncertainties. Following a re-determination of z for bismuth, in which it was found that the 1960 results were confirmed, the work was extended to determinations of z for alloys of Bi with Sb, and for Bi with small additions of Pb (an acceptor) and of Sn and Te (donors), using liquid nitrogen and liquid helium temperatures.

The dependence of the unit cell dimensions of Bi-Sb alloys on composition that was published by Jain (1959) was anomalous in the range between 4 and 8%, suggesting that these dimensions exhibit a strong influence of changing band gaps in this composition range. This dependence was also redetermined in the present work; the anomalies were not confirmed.

Material preparation

Starting with 99.998 to 99.999% purity bismuth from Cerro de Pasco Corporation, ingots were zone refined in vacuum in a fused silica boat. After 21 to 35 passes at 1 in. per hr. of a molten zone about 2 in. long (resistance furnace heating), no impurities were detected in the central parts of the ingots in spectrographic tests. The sensitivity of the tests was calibrated by standard samples made from the refined material, and in wt.% was estimated as follows: Fe 0.00001, Pb 0.0003, Mg 0.00001, Si 0.00001, Cu 0.00001, Ag 0.00001, Ni 0.001. In the last 2 or 3 in. of the ingots it was possible to see spectrographic traces of Cu, Ag and Ni; no impurities were seen at the starting ends of the ingots, but both ends were discarded. After etching the ingots in 50% HNO₃ and rinsing in distilled water, crystals were grown from them in a silica boat $\frac{3}{8}$ in. in diameter and 14 in. long, on which paraffin soot had been deposited. Some excellent crystals were grown except when the alloy contents were high in the Bi-Sb series of alloys.

Table 1. *Electrical resistance ratios of high purity bismuth single crystals*

Sample	$\frac{R_{300\text{ }^\circ\text{K}}}{R_{4.2\text{ }^\circ\text{K}}}$	$\frac{R_{300\text{ }^\circ\text{K}}}{R_{1.5\text{ }^\circ\text{K}}}$
Material as received	61 ± 0.4	68 ± 2
Zone refined, Friedman & Koenig (1960)	225 to 400	
Zone refined, this research	673 ± 3	1180 ± 100

A common test for purity is the ratio of electrical resistivity at room temperature to that at temperatures in the liquid helium range. A crystal tested in this way had the highest ratio yet reported for Bi (Table 1). In the course of these tests it was noted that straining the crystals greatly reduced the ratio; furthermore it is known (Friedman & Koenig, 1960) that maximum ratios are only obtained when samples

of sufficient size are tested. Since our crystal had the largest size of any we have seen reported, and was believed to have the lowest dislocation content, it would not be safe to conclude that our high resistance ratios necessarily proved a purity above all other crystals previously grown, though this may be the case.

Bi-Sb alloys were made from the central parts of the zone refined ingots of Bi using high purity Sb from Ohio Semiconductors, Inc. Spectrographic analysis of a 20 mg sample of the latter disclosed an estimated 0.0001% Cu, but no detectable trace of B, Mn, Pb, Au, Ta, Mg, Sn, As, Bi, Si, Fe, Zn, Al, Be, Mo, Ca, V, Ag, Zr, Co, Ni, Cd, Ti, or Cr. The alloy melts were given several zone levelling passes back and forth in vacuum, then single crystal portions in the central parts of the ingots were cut into appropriate lengths and cleaved. The cleavage surfaces least marked by cleavage steps and twins were chosen for use and were secured to the X-ray cryostat by soldering along one edge of the crystal (approximately $8 \times 8 \times 3$ mm.) with a low melting point solder. The surfaces X-rayed were always mirror like, permitting alignment by optical reflection; the high antimony content samples nevertheless had tear lines on the cleavage surface.

Analysis of the alloys

Wet chemical analyses were performed on samples (approximately 0.5 g.) adjacent to the X-ray specimens, using analytical methods described elsewhere: Jain (1959), Kolthoff & Lingane (1952), Lingane (1953), Wiberley *et al.* (1953). Some inhomogeneity in composition was found, particularly in the 8.4 and 15.7 at.% Bi-Sb alloys. Gross errors in the quoted compositions were avoided by X-ray fluorescence analysis of the actual cleavage faces of the crystals used for the experiments.

The alloys analyzed as follows, in at.-%: 3.1, 5.6, 8.4, 12.4, 15.6, 25.9, 27.8, 29.9 Sb; 0.15, 0.22 Te; 0.39 Pb, 0.125 Sn. A conservative estimate of the error in the quoted analysis of the most inhomogeneous alloy, the 8.4% Sb one, would place the composition in the range 7.9 to 8.9 at.% Sb. A more representative estimate of the error in the Bi-Sb series would be that for the 5.6% alloy, where the composition is considered to lie between 5.4 and 5.8% Sb. In the Te, Pb, and Sn alloys the errors may amount to 20% of the alloying element present.

Diffraction techniques

Lattice constants

The c dimensions (hexagonal cell) were determined from both single crystal and powder patterns, the a dimensions from powder patterns only. Ag $K\alpha$ radiation was used for most of the single crystal

measurements, but Co $K\alpha$ radiation was used for some of the room temperature measurements and for alloys of high antimony content because of the higher intensity in the high angle reflections obtained with this radiation. Only the 00- l reflections from the cleavage surface were utilized in single crystal measurements; the c dimensions were derived graphically, using the Nelson-Riley extrapolation function.

The powder samples were taken from positions on the ingots where chemical analyses had been made. The metal was ground in a mortar to pass through a 300 mesh sieve, sealed in pyrex glass capsules, and annealed for four to twelve hr. at 180 to 230 °C. in argon or in vacuum. Room temperature patterns were made on an 11.46 cm. diameter Bradley camera; a few also on a 10 cm. diameter symmetrical back-reflection focusing camera. The runs at 78 °K. were made on a General Electric diffractometer with a sample cooling attachment similar to that of Masson (1960). Measurements at helium temperature were made on the precision spectrometer and cryostat used for the intensity measurements of the following section.

Fe $K\alpha$ radiation was used for all powder patterns. In analyzing the diffractometer powder patterns the peak positions were found by the parabolic interpolation method of Booth (1948), and the lattice constants were calculated from the peak positions by the least squares method of Cohen (1936), using only the lines free from danger of overlap with neighboring lines. The wavelengths assumed were those of Cauchois & Hulubei (1947), converted to Å by the factor 1.00202. Where the $K\alpha$ doublet was not resolved (Bi-Sb alloys with more than 8.4% Sb) the weighted mean wavelength was used.

Parameter z

Integrated intensities were measured on a low temperature diffraction unit consisting of a cryostat, precision spectrometer, flat crystal monochromator, scintillation counter, pulse-height analyzer, scaler and recorder, as used in a previous study of bismuth (Barrett, 1960). The samples were single crystals cleaved on the (00-1) plane with the usable area of the cleavage plane being 5×7 to 10×12 mm. in size. The crystals were aligned optically, and the measurements carried out with the moving counter, moving crystal technique as before. Ag $K\alpha$ radiation was used throughout because of the many reflections it provides and the small dispersion correction required; care was taken to avoid the half wavelength component.

Thirteen 00- l reflections were available, but the 00-3, 00-6, 00-9, and 00-15 reflections were not used in deriving the results because their high intensities made them liable to large extinction errors; the 00-33 reflection was also given zero weight in the final calculations because its weakness made accurate

measurement impossible. At room temperature some other high order reflections also were too weak to be used.

The observed intensities were corrected by the Lorentz and polarization factors, including polarization by the monochromator crystal. The value of the z parameter was then refined by means of $(F_o - F_c)$ line syntheses (Lipson & Cochran, 1953) along the c axis, at points separated by 0.001 c and straddling the position of one of the atomic peaks in the cell. The scale factor was calculated by least square methods at each stage of the refinement. The structure deduced by James (1921) was assumed, and Barrett's (1960) z values as starting parameters.

In computing scattering factors for Bi-Sb alloys, the Brindley-James (1931) factors for Sb were combined with Bi values according to the atomic percentage of Sb; the small additions of other alloying elements did not require modification of the Bi values. The scattering factors for Bi used in the $(F_o - F_c)$ calculations were Freeman's (1959) values for Tl⁺, scaled up to give values for Bi (James, 1948), with a dispersion correction for K electrons only, called the f_1 curve in what follows. Of the other sets of scattering factors for elements of high atomic number in the literature, those of Worsley (1959) for Pb⁺⁺⁺, and Henry (1954) for Au⁺ and Hg⁺⁺, agree well with the Freeman values when correctly scaled, except at low $(\sin \theta)/\lambda$ values where the degree of ionization becomes of importance. The Thomas & Umeda (1957) values however decrease less rapidly beyond $(\sin \theta)/\lambda = 1$ than do those calculated from self-consistent field theory.

The changes in the results caused by using the Thomas-Umeda scattering factors for both Bi and Sb were examined; also the changes resulting from dispersion corrections considering other than the K electrons, using the Parratt & Hempstead (1954) theory and assumptions similar to those made by Dauben & Templeton (1955) in calculating dispersion corrections. The dispersion corrections for Ag $K\alpha$ radiation incident on Bi were found to be $\Delta f = -1.1$ for K electrons only, $\Delta f = -1.8$, $\Delta f' = 8.6$, by the Parratt-Hempstead theory. The corresponding values for Sb were -1.7 , -1.2 , and 1.0 respectively.

All the check calculations on the effect of using modified f curves were made by least squares methods, minimizing the function $\sum w(F_o^2 - F_c^2)$. Four modifications of the scattering curve were considered: the f_1 curve used for the difference synthesis, the same with added dispersion correction for other than the K electrons, f_2 ; the Thomas-Umeda curve with correction for K electrons only, f_3 , and for all electrons, f_4 . The f_1 and f_4 curves were found to differ most, and were used in most of the computations; the values of $|f_2|$ and $|f_3|$ were so similar that only the f_2 curve was used. The calculations were performed on an IBM 704 computer, using the Busing-Levy least-squares program (1959), and enabled a check to be made simultaneously on the effect of three schemes of

weighting the intensity data, counting the difference synthesis as one (Lipson & Cochran, 1953). The weights, w , assumed in most of the check calculations were derived using the equation

$$w = M/(I - Q),$$

where I is the observed integrated intensity, Q is the background count and M is the number of times the reading was repeated. The intense reflections were given zero weight, as in the $F_o - F_c$ syntheses, but the 00·33 reflection was included with the appropriate weighting. A few calculations were also made giving each reflection unit weight, and omitting the 00·33 and high intensity reflections.

Results

Lattice constants

The results are shown graphically in Figs. 1, 2 and 3, where the equations attached to the figures are the equations of the least squares straight lines drawn through the experimental points. All the results except those for pure antimony were used in deriving the equations, but the omission of the alloys of high Sb content, where the constants are less accurately known, does not significantly change the slopes or intercepts. Estimates of the standard errors of the slopes, calculated from the closeness of fit of the experimental points to the least squares lines are given in Table 2.

Straight lines between the values for Bi and our values for Sb have the same slopes as the observed ones for the a dimensions, within experimental error, but not for the c dimensions, as will be seen from the columns 'Expected m from Vegard's Law' and the standard deviations $\sigma(m)$ in Table 2. Therefore it is unjustified to extrapolate beyond present compositions with the linear equations given in Figs. 1, 2 and 3, especially for values of the c dimension.

The errors in the individual a and c constants were estimated from the spread of the duplicate results of the combined single crystal and powder data, and found to be, on the average, 0·005 Å or 1 part in 2,000 for the c dimension, with the same proportional error in the a dimension. The accuracy for the low Sb compositions was better than average. There is good agreement between our Bi and Sb lattice constant determinations and those summarized by Pearson (1958), including the thermal expansion values for Bi and Sb of Erling (1939). Less confidence can be placed in the thermal expansion coefficients of our high Sb alloys below 78 °K.

There is also satisfactory agreement between our rhombohedral a lattice constants of the Bi-Sb alloys, and the values found by Bowen & Morris-Jones (1932) and Ehret & Abramson (1934), after conversion to the primitive rhombohedral cell and changing to Å units. As can be seen from Fig. 4, however, the

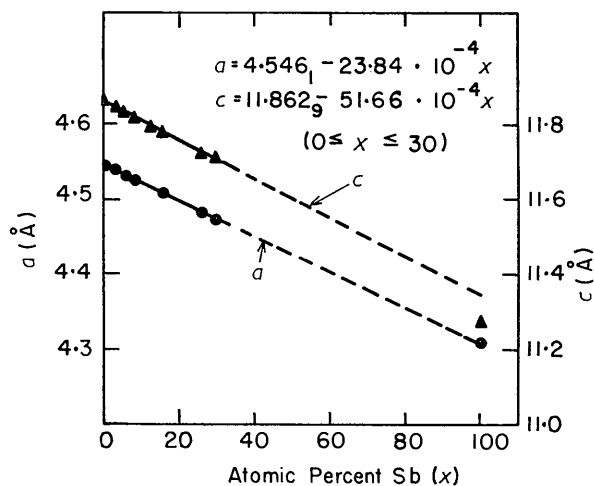


Fig. 1. Hexagonal lattice constants of Bi-Sb alloys at 298 ± 3 °K.

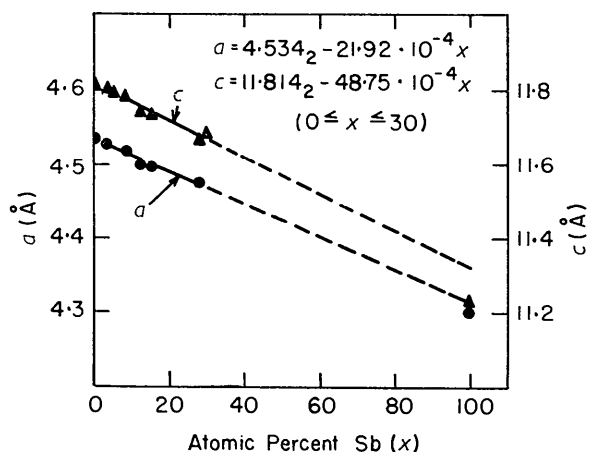


Fig. 2. Hexagonal lattice constants of Bi-Sb alloys at 78 °K.

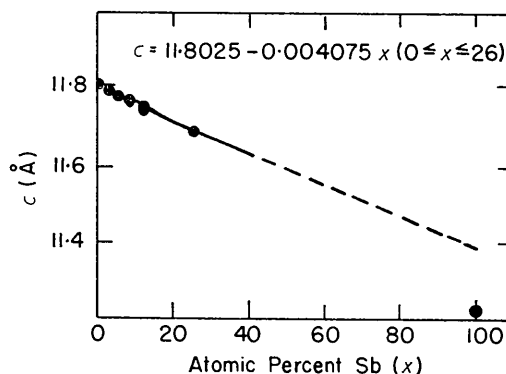


Fig. 3. Hexagonal lattice constant c of Bi-Sb alloys at 4.2 °K.

Table 2. Slopes, m , of parameter versus composition curves for Bi-Sb alloys, in Å per atomic percent Sb

Unit-cell dimension and temperature		m	Expected m from Vegard's law	$\sigma(m)$
c	298 °K.	-51.66×10^{-4}	-58.82×10^{-4}	0.90×10^{-4}
a	298	-23.84×10^{-4}	-23.77×10^{-4}	0.40×10^{-4}
c	78	-48.75×10^{-4}	-58.25×10^{-4}	3.46×10^{-4}
a	78	-21.92×10^{-4}	-23.44×10^{-4}	1.62×10^{-4}
c	4.2	-40.75×10^{-4}	-58.85×10^{-4}	1.48×10^{-4}

assumptions made by both pairs of workers, that the rhombohedral angle α varies linearly throughout the range from 0 to 100% Sb content, is inaccurate.

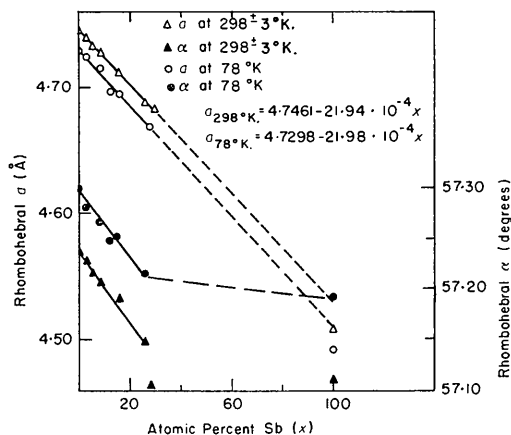


Fig. 4. Rhombohedral parameters of Bi-Sb alloys.

The lattice constants for pure Bi and Sb are given in Table 3. They differ slightly from the values deducible from Figs. 1, 2 and 3 and the Vegard's law slopes of Table 2. The values on Table 3 are the results of measurements on the pure elements only, whereas the values for $x=0$ in the equations of Figs. 1, 2 and 3 are the intercepts found by least squares methods (giving unit weight to each result) and depend on the

values found for the Bi-Sb alloys. The tabulated values are believed to be the more accurate ones.

Table 3. Lattice constants of pure Bi and Sb (Å)

		298 ± 3 °K.	78 °K.	4.2 °K.
Bi	c	11.862	11.814	11.797
	a	4.546	4.535	—
Sb	c	11.273	11.23	11.21
	a	4.308	4.30	—

The lattice constants of the Bi-Sn, Bi-Te and Bi-Pb alloys were found to be the same as those for pure Bi within the experimental error.

Atomic parameters

The final z parameters by the difference synthesis method are given in Table 4 for the Bi-Sb alloys and Table 5 for the Bi-Sn, Bi-Pb and Bi-Te alloys. Fig. 5 shows the variation of the z parameter with Sb concentration at low temperatures. The standard deviations of individual results, calculated from the deviations of duplicate results from their means, were found to be 25×10^{-6} (assuming that the variance is independent of composition, and considering data on all alloys at 78 and 4.2 °K.). There is not a sufficient number of duplicate results available to make a reliable estimate of the error at room temperature, but comparison of the results for different compositions indicate that it is two or three times as high.

Table 4. Temperature factors B and atomic z parameters of Bi-Sb alloys at 4.2, 78 and 298 °K.

Atomic % Sb	4.2 °K.			78 °K.			298 °K.		
	z	B	R (%)	z	B	R (%)	z	B	R (%)
0	0.23407	0.093	1.26	0.23400	0.321	2.78	0.23392	1.144	0.09
	—	—	—	—	—	—	0.23387	1.092	0.12
	—	—	—	—	—	—	0.23389	1.107	0.05
3.1	0.23406	0.104	1.09	0.23397	0.326	1.38	0.23388	1.22	2.93
	0.23404	0.126	1.86	0.23398	0.293	0.88	—	—	—
	0.23404	0.130	1.95	0.23402	0.365	1.37	—	—	—
5.6	0.23406	0.132	1.24	0.23400	0.336	0.95	0.23404	1.26	2.60
8.4	0.23403	0.112	1.21	0.23400	0.296	0.76	0.23396	1.34	3.75
	0.23409	0.131	1.76	—	—	—	0.23396	1.34	3.75
12.4	0.23402	0.098	0.86	0.23400	0.290	1.12	—	—	—
15.7	0.23410	0.177	0.58	0.23402	0.470	2.05	0.23399	1.37	2.37
25.9	0.23420	0.243	2.05	0.23409	0.378	1.80	0.23394	1.44	2.08
27.8	—	—	—	0.23411	0.307	0.70	—	—	—
	—	—	—	0.23407	0.290	2.03	—	—	—
29.9	0.23416	0.264	5.05	0.23413	0.365	1.69	—	—	—

Table 6 summarizes the results of calculations using different f curves and different computational methods; the standard errors for the Busing-Levy calculations are higher than those deduced from Table 5, presumably because in these the 00·33 reflection was given non-zero weight. Even if the higher estimates of errors are accepted, the trends in the z parameter are clear. Tables 4, 5 and 6 show that the value of z decreases with the increase of temperature in pure Bi and in all the alloys studied, and that z is independent of composition, except for the Bi-Sb alloys containing more than about 15% Sb.

Table 5. *Temperature factors B and atomic positional parameters z of solid solutions of Sn, Pb, and Te in Bi at 78 °K.*

Composition	z	B	R (%)
Bi 0·125% Sn	0·23400	0·296	1·57
	0·23399	0·291	1·80
Bi 0·39% Pb	0·23401	0·284	1·57
Bi 0·15% Te	0·23404	0·250	1·77
	0·23401	0·250	0·97
Bi 0·22% Te	0·23397	0·260	1·67
	0·23398	0·240	1·52

The new values for Bi at 78 and 4·2 °K. are in excellent agreement with the earlier findings by Barrett (1960), which were based on different crystals and used different computational methods. The comparable values are:

$$z = 0·23407 \text{ (new)} \quad 0·23406 \text{ (old) at } 4·2 \text{ °K.}$$

$$z = 0·23400 \text{ (new)} \quad 0·23401 \text{ (old) at } 78 \text{ °K.}$$

The new value at room temperature, 0·23398, differs from the 1960 value, 0·23401, and appears to be more consistent with the results on the Bi-Sb alloys but even at room temperature the difference between the old and new results is within the combined estimated errors.

Current theories are concerned with changes in the value of z with temperature and with the amount and kind (electron donor or acceptor) of alloying element, but do not predict absolute values. It is of importance therefore to consider whether or not the conclusions reached above, regarding the effects of temperature and composition on z , depend seriously on the atomic scattering curve used, or on the value of the dispersion correction adopted. From Table 6 it is clear that changing from the f_1 to the f_4 curve does tend to reduce the value of z by an amount almost equal to the standard error, for the alloys included in the table. The effect on temperature factors was found to be considerably greater, approximately 5 times the estimated standard error.

But it is seen from the table that for each individual f curve tested, the parameter z is not significantly changed throughout the composition range listed, either at 4·2 or at 78 °K., and the changes with temperature are also not significantly different for the different f curves. This is as would be expected from a consideration of the relationship between the f curves; the same is also true for higher Sb content alloys, as approximate calculations show.

As to effects that might arise from possible correlation of parameters (Geller, 1961), the following observations suggest that the interactions are small. There is good agreement between z values obtained on duplicate runs; there is good agreement when different weighting schemes are used on a given set of intensities; and there is monotonic convergence in the Busing-Levy calculations even when scale and temperature factors differing widely from the final values are used as starting parameters.

Our estimates of errors refer to precision rather than accuracy. Since the primary concern in the work is with changes in z with temperature and composition, it is the relative values that are of greatest importance; however, in view of the considerations

Table 6. *Comparison of various ways of computing z*

Method of calculation:		a		b		c			Standard errors		
f curve used:		f_1	f_1	f_2	f_4	f_1	f_2	f_4	$\times 10^6$ computed		
Parameter:		z_1	z_2	z_3	z_4	z_5	z_6	z_7	by method b		
Sample	Temp.								$\sigma(z_2)$	$\sigma(z_3)$	$\sigma(z_4)$
Bi	4·2 °K.	0·23407	0·23406	0·23404	0·23404	0·23404	0·23401	0·23398	29	42	41
Bi 3·1% Sb	4·2	0·23406	0·23405	—	0·23403	—	—	—	28	—	26
Bi 3·1% Sb	4·2	0·23404	0·23401	—	0·23400	—	—	—	45	—	55
Bi 3·1% Sb	4·2	0·23404	0·23413	—	—	—	—	—	58	—	—
Bi 5·6% Sb	4·2	0·23406	0·23406	—	—	—	—	—	27	—	—
Bi	78	0·23400	0·23394	0·23392	0·23392	0·23393	0·23388	0·23394	66	85	84
Bi 0·39% Pb	78	0·23401	0·23404	—	0·23401	—	—	—	47	—	34
Bi 0·125% Sn	78	0·23399	0·23397	—	0·23395	—	—	—	59	—	42
Bi 0·125% Sn	78	0·23398	0·23399	—	0·23396	—	—	—	42	—	48
Bi 0·22% Te	78	0·23397	0·23402	—	0·23399	0·23402	0·23403	0·23400	56	—	29
Bi 0·15% Te(A)	78	0·23404	0·23403	—	0·23401	—	—	—	32	—	45
Bi 0·15% Te(B)	78	0·23401	0·23405	—	0·23403	—	—	—	47	—	45
Bi 3·1% Sb	78	0·23398	0·23401	—	0·23400	—	—	—	33	—	49
Bi	298	0·23387	—	—	0·23385	—	—	—	—	—	44

a = Difference synthesis. b = Busing-Levy least squares program. c = Least squares, unit weights.

Table 7. Bond lengths and angles in Bi-Sb alloys

	Atomic % Sb								
	0	3.1	5.6	8.4	12.4	15.7	25.9	27.8	29.8
Bond lengths at 298 °K.									
Nearest neighbor (Å)	3.071	3.067	3.064	3.060	—	3.049	3.031	—	—
2nd nearest neighbor (Å)	3.529	3.525	3.517	3.514	—	3.501	3.483	—	—
Bond angles at 298 °K. (degrees)									
Nearest neighbor	95.484	95.482	95.392	95.420	—	95.394	95.386	—	—
2nd nearest neighbor	80.198	80.184	80.236	80.196	—	80.194	80.130	—	—
Bond lengths at 78 °K.									
Nearest neighbor (Å)	3.064	3.059	<i>3.055</i>	3.054	3.042	3.041	<i>3.027</i>	3.025	<i>3.024</i>
2nd nearest neighbor (Å)	3.516	3.512	<i>3.507</i>	3.506	3.492	3.490	<i>3.473</i>	3.470	<i>3.469</i>
Bond angles at 78 °K. (degrees)									
Nearest neighbor	95.476	95.466	<i>95.462</i>	95.456	95.438	95.428	<i>95.368</i>	95.406	<i>95.296</i>
2nd nearest neighbor	80.304	80.282	<i>80.288</i>	80.272	80.252	80.266	<i>80.260</i>	80.312	<i>80.216</i>

Italicized entries based on interpolated a or c constants.

mentioned above, we judge the absolute errors are not more than two or three times the standard errors we have listed.

Temperature factors

The B values are more affected than are the z values by crystal imperfections, crystal missetting and instrumental drifts, and consequently are less accurately known. The standard errors in B as estimated by the Busing-Levy program average 0.0096 at 4.2 °K. and 0.0136 at 78 °K., and do not differ greatly from alloy to alloy, among those listed in Table 6. The precision estimated from duplicate results by the ($F_o - F_c$) synthesis method is of the same order of magnitude (Tables 4 and 5) except for the 3.1% Sb alloy at 78° where the spread is considerably greater.

Interatomic distances

Table 7 lists bond lengths and interbond angles. The errors in these are variable, and depend more on the errors in the chemical analysis and lattice constant measurements than on the atomic coordinates, except in the case of pure Bi, where the lattice parameters are known to 1 part in 10,000 with some certainty. The standard errors for the first neighbor interatomic distances in Bi, assuming an error of 1 in 10,000 in the lattice constants and $(z) = 5 \times 10^{-5}$ and 1×10^{-4} at 78 and 298 °K. respectively, are 6×10^{-4} and 12×10^{-4} . (The $\sigma(z)$ values were chosen large to cover uncertainties in the f curves used.)

Reliability factors, R

These are the usual values of $\Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ and are included in Tables 4 and 5 as an indication of the accuracy of our intensity determinations.

Discussion

The abrupt deviations of Bi-Sb lattice constants from linear dependence on composition below 8 at.% that

were reported by Jain (1959) were not found in the present work, which we believe to be more precise. There is, however, a small positive deviation from a straight line relationship between the pure metals for the c dimensions and for unit cell volumes. This is opposite in direction to the deviations that might be expected if a point of view proposed by Friedel (1955) is applied to this system.

Present results confirm the finding by Barrett (1960) that z decreases with increasing temperature in Bi and show that similar behavior is found in the alloys. Since the atoms in the Bi structure lie on planes separated, alternately, by $(2z - \frac{1}{3})c$ and $(\frac{2}{3} - 2z)c$, the effect of raising the temperature is to expand the larger of these two spacings faster than the smaller, a not unreasonable result. The change of z with temperature is in the wrong direction to be accounted for by the Blount-Cohen model; perhaps the number and mass of the thermally excited electrons are too small to provide the control of z that was postulated and another factor exerts the control (Barrett, 1960). Seeking an understanding of the observation that additions of Sn, Te and Pb leave z unchanged, whereas additions of more than 13% Sb raise z , Cohen (1961, unpublished) has made the following suggestion. The number and the mass of electrons contributed by small alloying additions may be too small to exert control, but perhaps the addition of more than 13% Sb shifts the bands so as to bring about a new band overlap that involves heavy mass bands capable of increasing z as observed (Fig. 5) and at the same time decreasing residual resistivities as observed by Jain (1959).

If the temperature factor B for the Bi-Sb alloys in Table 4 is viewed as the sum of a component B_T from thermal vibrations added to a component B_s (nearly temperature independent) from the local strains caused by fitting together atoms of different size (Borie, 1957; Herstein *et al.*, 1956), the data imply that B_T increases with Sb content; likewise the increase in B at 4.2 °K., where B_T must be very

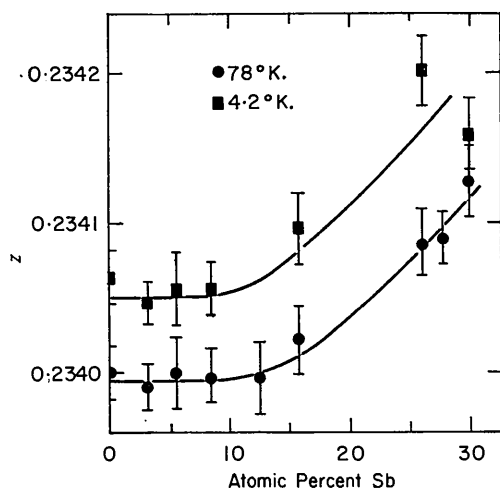


Fig. 5. Atomic parameters z of Bi-Sb alloys at 78 and 4.2 °K. Mean values of z are plotted where two or more results are available. Estimated standard errors are indicated.

small, also indicates an increase in B_s with Sb content. Attempts to draw quantitative conclusions regarding these components are hindered by the scatter of the observed values, the dependence of these on the f curve used, and the many assumptions involved in even an approximate theory.

In pure Bi, B depends strongly on the f curve used: at 4.2 °K., for example, the B obtained in using the f_1 curve is 0.079 (Busing-Levy computation), 0.081 (least squares computation with unit weighting) and 0.093 ($F_o - F_c$) synthesis, as contrasted with the values obtained in using the f_4 curve and the first two computing methods, 0.142 and 0.147 respectively. If it becomes possible to make reliable theoretical calculations of B this strong dependence might then be used to test the validity of different f curves.

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Note added in proof: The lattice constants a and c for Sb at 78 °K. and 4.2 °K. (Table 3) are believed to be less accurate than all the others and are being

redetermined with a higher precision method, together with z for Sb at various temperatures.

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