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Elastic constants of lead-bismuth alloys

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Abstract. A study of ultrasonic velocities and internal friction has been carried out in Pb-Bi alloys in the concentration range of 0 to 49·5 atomic% Bi using the composite oscillator technique. From the velocity and density data a set of elastic constants namely, Young's modulus, rigidity modulus, bulk modulus and Poisson's ratio are estimated. The results are interpreted in terms of the phase changes occurring in the alloy system. Internal friction is found to be more sensitive than the elastic constants to the phase changes.

Keywords. Ultrasonic velocities; Young's modulus; rigidity modulus; Poisson's ratio; bulk modulus; internal friction.

1. Introduction

The phase diagram of the Pb-Bi system has been widely investigated (Hansen 1958). Various physical properties such as Hall effect, electrical resistance and density (Thomas and Evans 1933) have been studied. Kuczynski and Norton (1948) have investigated the Young's modulus and strain coefficients of resistivity of Bi-Pb alloys in the concentration range of 0 to 2·5 atomic% Pb using a static method. Lattice spacings of Pb rich solid solution with Sb, Bi, Sn, In, Tl, Cd and Hg have been reported (Tyzack and Raymor 1954) and it has been found that only Bi expands the Pb lattice. Recently Anderson *et al* (1975) have reported the de Haas-Alphen effect of dil Pb-Bi alloys. Though extensive ultrasonic studies have been carried out in Pb based alloys (Subrahmanyam 1972), no attempt has been made so far to study the effect of phase changes on ultrasonic velocity and elastic constants of the Pb-Bi alloy systems. Hence the present investigation of Pb-Bi alloys in the concentration range of 0 to 49·5 atomic% Bi is taken up to study the effect of phase changes on ultrasonic properties.

2. Experimental details

The method of preparation of the samples and testing of isotropy were the same as reported earlier (Gopinathan and Padmini 1974). The polycrystalline alloy specimens were prepared using 99·99% pure Bi (NFC, India) and 99·95% pure Pb (Riedel, Germany). From the large homogeneous polycrystals three specimens were cut in three different directions. The surfaces of the alloy specimens were observed using a Vicker's projection microscope after etching ($CH_3COOH : HNO_3 : H_2O$; 3 : 4 : 6).

Metallographic examinations were made on the alloys after polishing. The actual impurity content of the samples was estimated from the density measurements by the Archmedean method, to an accuracy of 10^{-4} g cm^{-3}. Ultrasonic velocities, internal friction and density of the three specimens from the same sample showed the same values which confirmed the isotropic and homogeneous nature of the alloys. All the samples were annealed in vacuum at 100°C for a period of 48 hr for homogenisation.

Ultrasonic wave velocities and internal friction are carried out at room temperature (29°C) using the composite oscillator technique originally developed by Balamuth (1934). The RF output of 1 V from a Radart (type 925) signal generator is amplified to 100 V and applied to the quartz transducer by means of a shielded cable. The output voltage across the crystal is then applied to a Simpson (727-I) vacuum tube voltmeter. The frequency of the signal generator is varied by a slow motion drive. The amplitude of the current which flows through the quartz varies critically with frequency (Seigel and Quimby 1936; Zacharias 1933), in the neighbourhood of certain resonance frequencies at which the amplitude passes through a maximum. The current flowing through the crystal is proportional to the voltage across a resistance (Sutton 1953) connected in series with the crystal and this voltage can be measured with a VTVM. If f_1 denotes one of these frequencies then at a frequency f' slightly less than f_1, the voltage passes through a maximum and at a frequency f'' slightly greater than f_1 it passes through a minimum. If V' and V'' denote respectively the maximum and minimum values of voltage amplitude then f_1 the resonance frequency of the transducer is given by

$$f_1 = f' + \frac{V''(f'' - f')}{V' + V''}.$$

The transducer is cemented to the specimen by a suitable bond (Salol) and the resonance frequency of the composite system is determined (f_0). Under the condition that all the frequencies are nearly equal ($\pm 10\%$) the resonance frequency of the specimen (f_r) can be obtained by the equation (Birch 1950)

$$f_r = f_0 + (f_0 - f_1)\, m_1/m_2,$$

m_1 and m_2 are the masses of the transducer and specimen respectively. The frequency is measured using an Apalab (type 1102) digital frequency counter to an accuracy of 1 in 10^6. The length of the specimen is determined using a comparator with an accuracy of 0·001 cm. An X-cut quartz rectangular bar crystal of fundamental frequency 110 kHz is used for longitudinal waves and a Y-cut cylindrical quartz crystal of fundamental frequency 120 kHz is used for shear waves. The velocity measurements are accurate to 0·1% while the modulus values are accurate to 0·2%.

The internal friction measurements are carried out using the same technique (Marx 1951) with the X-cut quartz crystal. The amplitudes of vibration are noted for different frequencies including the resonance frequency and the resonance curve is drawn. From this curve the frequency f_{max} corresponding to maximum amplitude, and the frequencies f_1 and f_2 on either side of resonance corresponding to

half the maximum amplitude are noted. The internal friction is estimated from the formula (Postnikov *et al* 1967)

$$\phi^{-1} = \frac{\Delta f}{f_{\max}\sqrt{3}} \text{ where } \Delta f = f_2 - f_1.$$

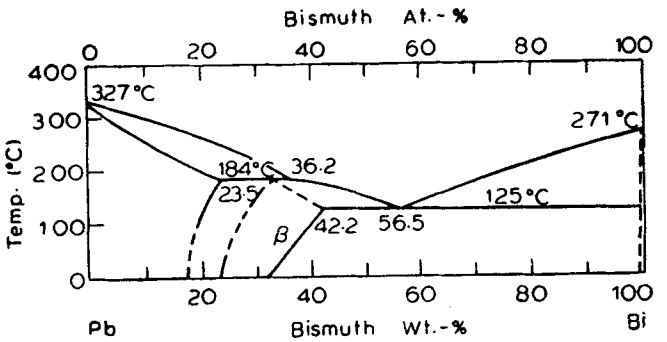

Figure 1. Phase diagram of Pb-Bi system (Hansen 1958)

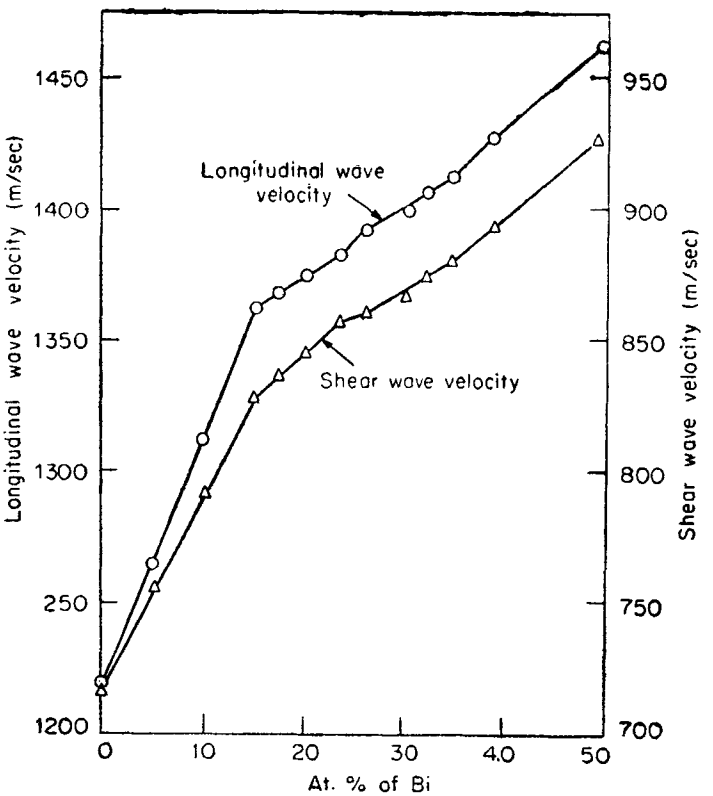

Figure 2. Concentration dependence of V_L and V_S

The width of the resonance curve varied from 0·1707 kHz for pure Pb 0·0854 kHz for the alloy containing 49·5 atomic % Bi in our experimental results. The accuracy of internal friction is about 6 to 8%.

3. Results and discussion

From the resonance frequencies, the longitudinal wave velocity V_L and shear wave velocity V_S are estimated. The various elastic constants such as—Young's modulus E, shear modulus n, Poisson's ratio σ and bulk modulus K are calculated from the formulae

$$E = \rho V_L^2 \; ; \; n = \rho V_S^2$$

$$\sigma = \frac{E-2n}{2n} \; ; \; K = \frac{E}{3(1-2\sigma)}$$

where ρ is the density of the material. All the results are presented in table 1 and in figures 2, 3, 4 and 5. The values reported are the average ones from the specimens

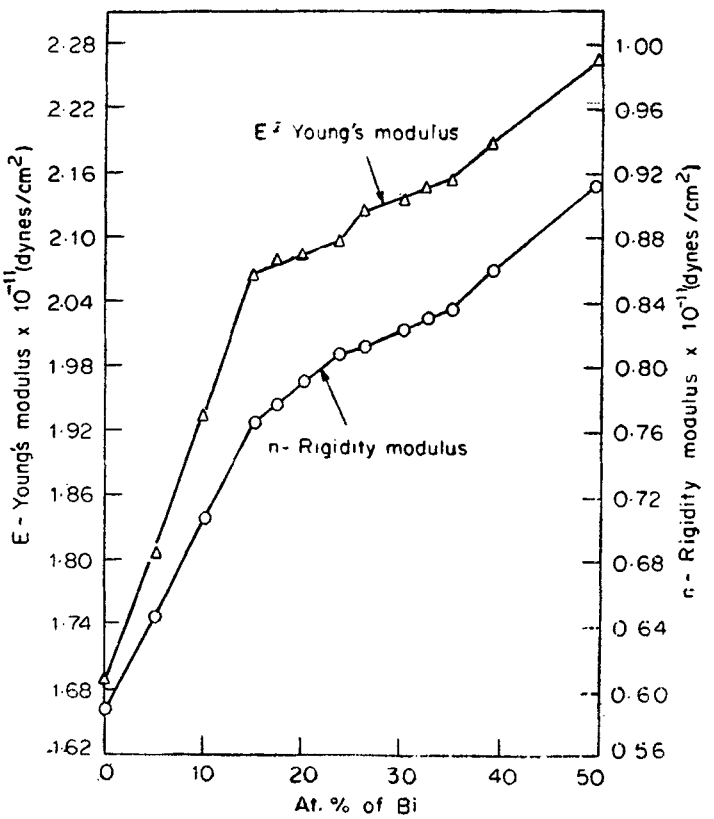

Figure 3. Concentration dependence of E and n

Table 1. Ultrasonic velocities, elastic constants and internal friction of Pb-Bi alloy system

Pb + Bi at. %	Density ρ g/cc	Longitudinal wave velocity V_L m/sec	Shear wave velocity V_S m/sec	Young's modulus $E \times 10^{-11}$ dynes/cm^2	Rigidity modulus $n \times 10^{-11}$ dynes/cm^2	Bulk modulus $K \times 10^{-11}$ dynes/cm^2	Poisson's ratio σ	Frequency corresponding to maximum amplitude f_{max} kHz	Width of the resonance curve Δf kHz	Internal friction $\phi^{-1} \times 10^4$
Pure Pb	11·387	1218	717	1·689	0·585	5·027	0·444	107·186	0·1707	9·196
5·1	11·281	1265	755	1·805	0·643	3·134	0·404	109·738	0·1429	7·518
9·8	11·215	1313	793	1·933	0·705	2·497	0·371	111·102	0·1202	6·246
15·1	11·138	1363	828	2·069	0·764	2·362	0·354	108·386	0·0976	5·202
17·1	11·094	1368	837	2·076	0·777	2·110	0·336	112·473	0·0922	4·731
19·98	11·045	1374	846	2·085	0·791	1·909	0·318	109·117	0·1084	5·738
23·3	10·987	1382	857	2·098	0·807	1·748	0·300	108·297	0·1172	6·248
26	10·952	1393	861	2·125	0·812	1·845	0·308	110·817	0·1176	6·125
30·25	10·906	1399	868	2·135	0·822	1·770	0·299	107·285	0·1101	5·928
32·25	10·851	1407	874	2·148	0·829	1·755	0·296	113·389	0·1130	5·753
35	10·808	1412	879	2·155	0·835	1·710	0·290	111·934	0·1065	5·496
39	10·748	1427	894	2·189	0·859	1·614	0·274	108·516	0·1114	6·926
49·5	10·607	1462	928	2·266	0·913	1·458	0·241	109·381	0·0854	4·508

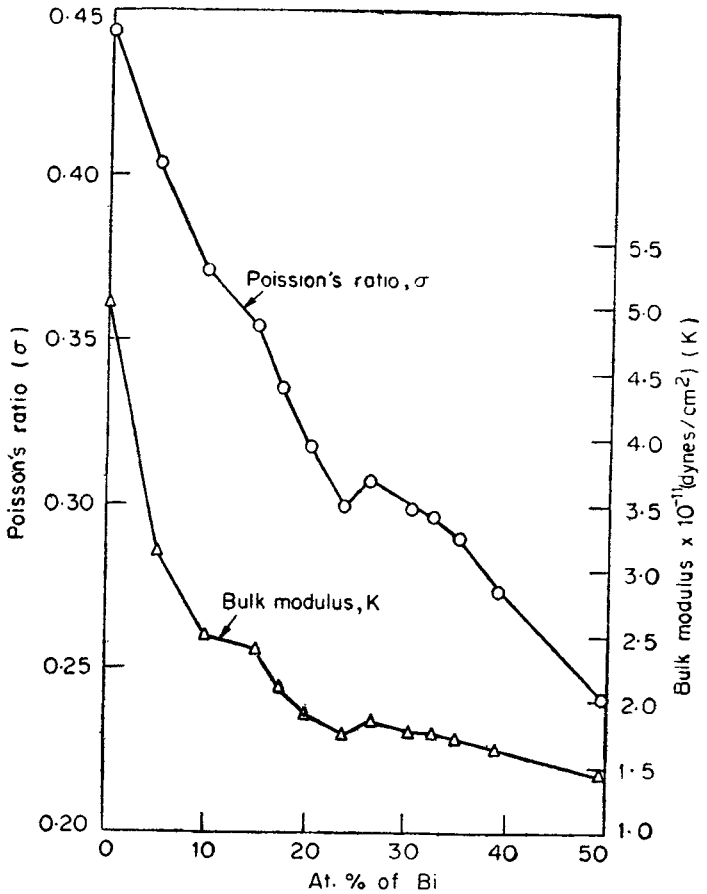

Figure 4. Concentration dependence of K and σ

cut in various directions. The elastic constants for pure Pb agrees well with the values reported (Kaye and Laby 1959).

A study of the phase diagram (figure 1) shows that the system Pb-Bi consists of (1)α, the f.c.c. Pb rich solid solution (0 to 17 atomic % Bi) (2) $\alpha + \beta$ phase (17 to 23 atomic % Bi), (3) β, the hexagonal close packed intermediate phase (23 to 35 atomic % Bi), (4) $\beta + \gamma$ phase (35 to 98 atomic % Bi) and (5) the bismuth rich rhombohedral solid solution, γ. From figure 2 it can be seen that at first both the longitudinal and shear wave velocities show a rapid increase upto 15·1 atomic % Bi and there is a change of slope in the neighbourhood of 15·1 atomic %. According to the phase diagram the alloy changes from a single phase α to a mixed phase $\alpha+\beta$ at about 17 atomic % Bi. The change in slope at 15·1 atomic % can be attributed to the pretransitional effects which are developed just before a phase change occurs. Solomon and Jones (1931) have investigated the crystal structures in Pb-Bi alloys at different concentrations and found that the addition of Bi upto 20 atomic % causes an expansion of the lattice from $a = 4{\cdot}930$ Å to $a = 4{\cdot}946$ Å. They have reported that at about 20 atomic % Bi concentration the hexagonal close packed structure begins to appear besides the f.c.c. structure of Pb. As the percentage of Bi increases from 20 to 25 atomic % Bi the crystal structure generally transforms

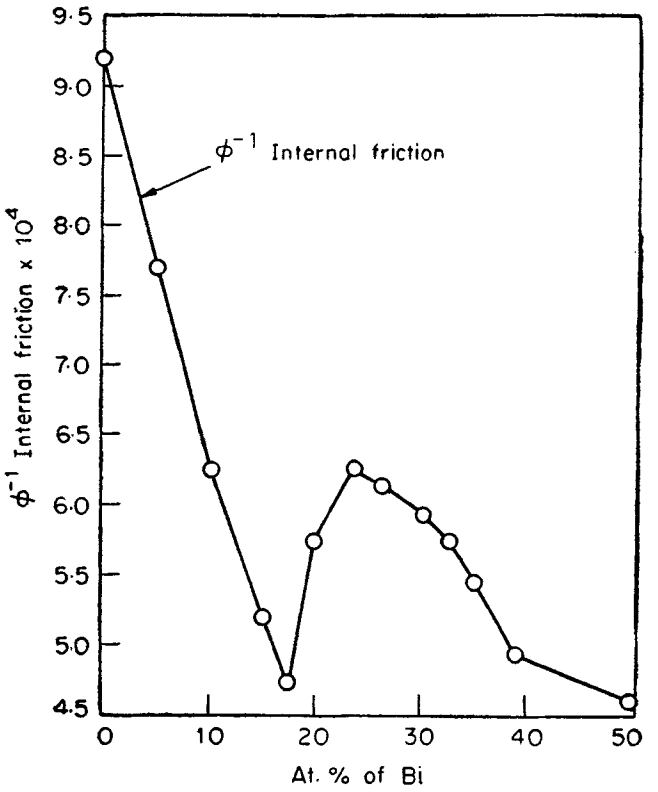

Figure 5. Concentration dependence of ϕ^{-1}

from f.c.c. to hexagonal close packing at 25 atomic % Bi. In the ultrasonic velocity values, a slight change or kink is observed at 23·3 atomic % Bi and this can be attributed to the initiation of change in phase from $\alpha + \beta$ to β. This kink is more prominent in longitudinal wave velocity, while it is less in shear wave velocity. Investigations by Preece and King (1969) have revealed that in the concentration range of 26·5 to 38·3 atomic % Bi the lattice parameter at 303°K, increases from $a = 3{\cdot}5021$ Å to $a = 3{\cdot}5081$ Å, while the axial ratio c/a increases from 1·6535 to 1·6550. It is interesting to note that in this concentration range both the ultrasonic wave velocities show a gradual increase with increasing concentration of Bi from 26 to 35 atomic % and at 35 atomic % there is a very slight change in slope in longitudinal wave velocity while it is not so prominent in shear wave velocity. This change in slope can be attributed to the change of phase from β to $\beta + \gamma$. In the range of 35 to 49·5 atomic % Bi the wave velocities have shown gradual increase with increase of concentration of Bi.

A study of the results on Young's modulus E and rigidity modulus n (figure 3) shows that just before the alloy system changes from α to $\alpha + \beta$ a change in slope in both the elastic constants is observed though the change in slope in E is more prominent than in n. When the alloy system changes from $\alpha + \beta$ to β, E has shown a sharp rise while the rigidity modulus has shown again a change in slope. Both of them vary regularly throughout the β phase. When the alloy system changes from β to $\beta + \gamma$ again there are kinks in both E and n values. In the concentration range of 35 to 49·5 at m % the elastic constants have shown a linear increase.

A study of the variation of bulk modulus K and Poisson's ratio σ (figure 4) with increase of concentration of Bi in various phases shows that the values of K and σ exhibit irregular variation in the vicinity of phase transition points.

From figure 5 it can be seen that the internal friction ϕ^{-1} is more sensitive than the elastic constants to the phase changes occurring in the system. At first ϕ^{-1} decreases and shows a minimum at 17 atomic% Bi. From 17 to 23·3 atomic% Bi it shows an increase. This sudden change in internal friction can be attributed to the phase change from α to $\alpha + \beta$. At 23·3 atomic% there observed a maximum where there is a phase change from $\alpha + \beta$ to β. A change in slope can be seen at 39·5 atomic% Bi which can be attributed to the post-transitional effects which lead to more fluctuations and thus affect the internal friction values.

Thomas and Evans (1933) investigated the resistivity and reported that if the resistivity curve was plotted on a larger scale there was evidence of slight discontinuities in the neighbourhood of 20%, 25% and 33% Bi. They attributed these discontinuities to the phase changes occurring in the system. Our results on ultrasonic velocities, Young's modulus and rigidity modulus confirm their investigations.

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