JOURNAL OF MATERIALS SCIENCE 6 (1971) 1331–1337

# Magnetic Susceptibilities and Single Crystalline Elastic Constants of Lead-Indium Alloys*

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The magnetic susceptibilities and single crystalline elastic constants of lead-indium alloys have been measured in the composition range 0 to 20 at.% indium. Comparison of these data with the data from lead-thallium alloys shows that, in the composition range 0 to 7 at.% solute, the solutes serve primarily to deplete the valence electron concentrations with band structures which are essentially the same as that of pure lead. At higher solute concentrations, those parameters of the lead-indium alloys which are controlled by the valence electron distributions diverge from values which would be expected from a simple lowering of the Fermi energy within the band structure of lead. Thus a rigid band approximation is valid at lower but not at higher indium concentrations in the lead-indium system. A qualitative correlation exists between the elastic anisotropy ratios and the stacking fault densities in both the lead-indium and lead-thallium alloy systems.

## 1. Introduction

At the present time there is available a great deal of experimental and theoretical information concerning the Fermi surfaces and band structures of elemental metals, but, primarily because of the experimental limitations for the determination of Fermi surfaces, there is very little information concerning the Fermi surfaces and band structures of alloys. Such data for alloys are essential both in studies of solution-hardening and to the development of an understanding of the nature of atomic bonding in multicomponent metals.

Gold [1] has made de Haas-van Alphen measurements on lead. Anderson and Gold [2] subsequently extended these measurements and determined the geometry of the Fermi surface and the band structure of lead. Their results show the Fermi surface of lead to be closely approximated by the free electron model with only minor deviations from sphericity near the Brillouin zone boundaries. Shepard and Smith [3] have measured the elastic constants of fcc lead-thallium alloys in the temperature range 4.2 to 300°K. Their results show a minimum in the compositional dependence of $\frac{1}{2}(C_{11}-C_{12})$ near 60 at. % thallium which reflects a maximum in the shear anisotropy $2C_{44}/(C_{11}-C_{12})$. This behaviour was found at all temperatures within the range of measurements and is explicable in terms of the electronic structure of lead with a rigid band approximation. The rigid band approximation in this sense simply means that the band structure of lead is valid for the alloys and that addition of thallium to lead decreases the valence electron concentration and depresses the energy value at the Fermi surface. Thus the evidence is that the electron distributions in lead-thallium alloys are also closely approximated by the free electron model.

The present work was stimulated by the fact that indium and thallium possess the same group valency and lead-rich lead-indium alloys, like the lead-rich lead-thallium alloys, crystallise

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*The work was performed in the Ames Laboratory of the US Atomic Energy Commission. Contribution No. 2950.

with the fcc structure. This structural correspondence requires identical Brillouin zone geometries and symmetry constraints. The correspondence in valency causes equivalent indium and thallium concentrations to generate identical electron-to-atom ratios. However, the volume per atom for indium is appreciably less than that for thallium, and equivalent indium and thallium concentrations have significantly different valence electron densities in real space. Thus measurements of the elastic behaviour of fcc lead-indium alloys were undertaken in order to provide data which could be compared with lead-thallium data at equivalent electron/atom ratios but with different electronic densities in real space.

Further, since the Pauli paramagnetism of an alloy is in the nearly-free-electron model proportional to the density of states at the Fermi level, measurements of the magnetic susceptibilities of lead-indium and dilute lead-thallium alloys were also undertaken. Mathematically, the density of states at the Fermi level is the reciprocal of the energy gradient in wave number space integrated over the Fermi surface [4]. Thus a comparison of the magnetic susceptibilities of the two alloy systems can indicate similarities or differences in their electronic distributions and should correlate with the elastic behaviour.

Finally, one of us has been interested in the mechanical behaviour of these lead alloys, and an additional motivation for the elasticity measurements was to test for relationships between the elastic behaviour and other mechanical parameters. Such a relationship in the form of a qualitative correlation between stacking fault densities and elastic anisotropy ratios was established.

## 2. Procedure and Results

### 2.1. Elastic Constants

Indium and lead were both obtained from Cominco, Inc., the supplier's specification of purity being 99.999%. For the growth of single crystals for the elastic constant measurements, appropriate amounts of these elements were first weighed and sealed in tantalum crucibles. To prevent oxidation, the tantalum crucibles were in turn sealed in stainless steel cylinders. These operations were performed under reduced pressures of $\sim 5 \times 10^{-6}$ torr. The samples were then melted and homogenised by agitation for 15 h in a rocking furnace at 50°C above the melting point of the specific alloy. Single crystals of the alloys were grown by the Bridgman technique in which the samples were solidified in sharply pointed tantalum crucibles by lowering through a steep temperature gradient at a rate of $< 2$ cm/h. Light reflection patterns, after etching with a solution of ammonium molybdate in dilute nitric acid [5], confirmed that the alloys were single crystals. The individual crystals were oriented by the Laue back-reflection X-ray method, and specimens were spark-cut to produce two parallel $\{110\}$ planes approximately 0.6 to 1 cm apart. These parallel faces were first hand-lapped and then electropolished [6] in a solution of 6% perchloric acid and methyl alcohol at $-70$°C with a current density of about 2 A/cm$^2$. This electropolishing was applied for 1 min at 50 V and was followed by a cleaning in alcohol. The process was repeated until a bright surface was obtained. Chemical analyses were made on portions of the crystals which were removed during spark-cutting. The results of these analyses are included in table I.

**TABLE I** Composition of lead-indium alloys

| Nominal at. % indium | Chemical analyses, at. % indium |
|---|---|
| A. Single crystals | |
| ~5 | 5.5 |
| ~10 | 9.0 |
| ~20 | 20.7 |
| B. Polycrystals | |
| ~5 | 4.4 |
| ~9 | 8.5 |
| ~14 | 12.8 |
| ~17 | 16.8 |
| ~21 | 20.8 |
| ~24 | 24.0 |
| ~31 | 30.5 |
| ~36 | 37.6 |
| ~38 | 37.3 |
| ~42 | 43.5 |
| ~44 | 43.6 |
| ~49 | 49.3 |
| ~50 | 49.8 |

It has been reported earlier [7] that no success was achieved with the Bridgman technique during attempts to grow single crystals of lead indium alloys at indium concentrations much greater than 20 at.%, and in the present investigation elastic data are for three single crystals containing 5.5, 9.0, and 20.7 at. % indium at fixed temperatures of 78°K, ~ 200°K, and 300°K. Elastic constants were determined through use of the pulse-echo technique. Pulses were generated at 10 MHz which was the resonant frequency of the X-cut and Y-cut quartz transducers which were employed. Measurements at room temperature were made with the transducers bonded to the test specimens with Salol. Measurements at 78°K were achieved with a liquid nitrogen bath and near 200°K with a dry ice-acetone bath. For these low-temperature measurements, Nonaq stopcock grease was used for bonding the transducers to the test specimens. The apparatus and technique have previously been described [3, 8]. Values for transit times of pulses through the test specimens could be combined with specimen dimensions to evaluate ultrasonic wave velocities. For wave propagation in the [110] direction the velocities of the three independent modes are related to the conventional elastic constants in the following way:

$$\rho v_t^2 = C_{44},$$
$$\rho v_{t'}^2 = \tfrac{1}{2}(C_{11}\text{-}C_{12}) = C',$$
$$\rho v_L^2 = \tfrac{1}{2}(C_{11} + C_{12} + 2C_{44}) = C_L,$$

where $v_t$ is the velocity of the shear wave polarised in the [001] direction, $v_{t'}$ is the velocity of the shear wave polarised in the [1$\bar{1}$0] direction, $v_L$ is the velocity of the longitudinal wave, and $\rho$ is the density. Values for the densities of the lead-indium alloys have been taken from the work of Rider and Roney [9]. Because no values were available for thermal expansion coefficients of these alloys, dimensional contraction occurring between room temperature and 78 or 200°K was neglected. Such neglect should generate no error in the elastic constant values greater than 0.2 to 0.3 %, which error is comparable to the experimental precision. Fig. 1 shows the experimentally determined elastic constants as functions of temperature. Values for the conventional elastic constants $C_{11}$, $C_{12}$, and $C_{44}$ are listed in table II. In both the figure and the table, the data for pure lead of Waldorf and Alers [10] are incorporated for comparison.

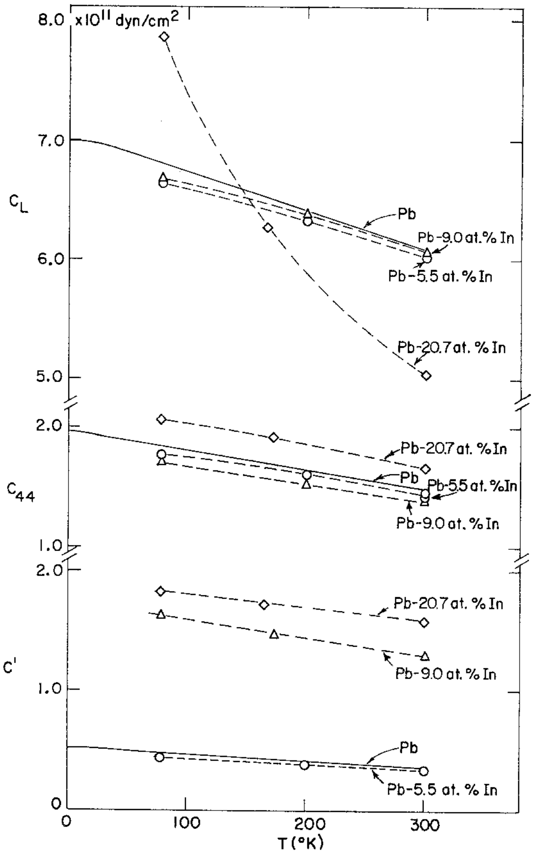

*Figure 1* Temperature variation of the directly measured elastic constants of lead-indium alloys at various compositional parameters.

TABLE II Elastic constants of lead-indium alloys in units of $10^{11}$ dymes/cm$^2$

| T°K | Constant | 0 at. % In | 5.5 at. % In | 9.0 at. % In | 20.7 at. % In |
|---|---|---|---|---|---|
| 78 | $C_{11}$ | 5.435 | 5.325 | 6.600 | 7.635 |
| | $C_{12}$ | 4.495 | 4.445 | 3.340 | 3.975 |
| | $C_{44}$ | 1.833 | 1.765 | 1.710 | 2.055 |
| 200 | $C_{11}$ | 5.169 | 5.110 | 6.339 | 5.673 |
| | $C_{12}$ | 4.343 | 4.330 | 3.389 | 2.343 |
| | $C_{44}$ | 1.646 | 1.610 | 1.531 | 1.867 |
| 300 | $C_{11}$ | 4.953 | 4.932 | 5.970 | 4.870 |
| | $C_{12}$ | 4.229 | 4.251 | 3.370 | 1.890 |
| | $C_{44}$ | 1.490 | 1.443 | 1.390 | 1.660 |

### 2.2. Magnetic Susceptibilities

For the magnetic susceptibility measurements the lead and indium were taken from the same stock as was used in the preparation of the single crystals. Thallium was also used and was obtained from the Leytess Corp. with the producer's specification of purity again being 99.999%. Polycrystalline alloy specimens were produced by pouring molten metal into graphite moulds. The poured metal was stirred continuously during the operation, and a flowing argon atmosphere provided an inert environment. Chemical analyses of these polycrystalline samples are shown in the second portion of table I. Microprobe analyses were also performed on arbitrarily selected specimens. In these analyses, scans were made across the surfaces of the test specimens. The results showed that the "as cast" samples were inhomogeneous on a small scale. The compositional traces were observed to oscillate with variable amplitudes as the microprobe scanned across the sample, but the oscillations for the two components were exactly out of phase so that a region rich in lead was poor in indium and vice versa. It was found that homogenisation was achieved by annealing the samples at temperatures within 50° of the solidus temperatures for periods of the order of six days. Microprobe scans after such annealing treatment showed compositional traces which were flat within the resolution of the instrument. All specimens were therefore given such an annealing treatment.

Magnetic susceptibilities were determined with the Faraday technique. The procedure and apparatus have been described in an earlier publication [11]. Data over an extensive composition range were taken only at room temperature; however, a limited number of measurements on selected samples (including alloys containing 8.7 and 20.5 at. % indium) over the temperature range 80 to 300°K showed only weak variations with temperature of the magnetic susceptibilities with no abnormalties; the variations are similar in magnitude and character to the behaviour of pure lead. The measured magnetic susceptibilities are thus expected to contain only a Langevin diamagnetic contribution from the ion cores and a contribution from the conduction band. Experimental points for both the lead-indium and lead-thallium alloys are plotted as functions of composition in the lower portion of fig. 2. Data from fragments which were spark-cut from

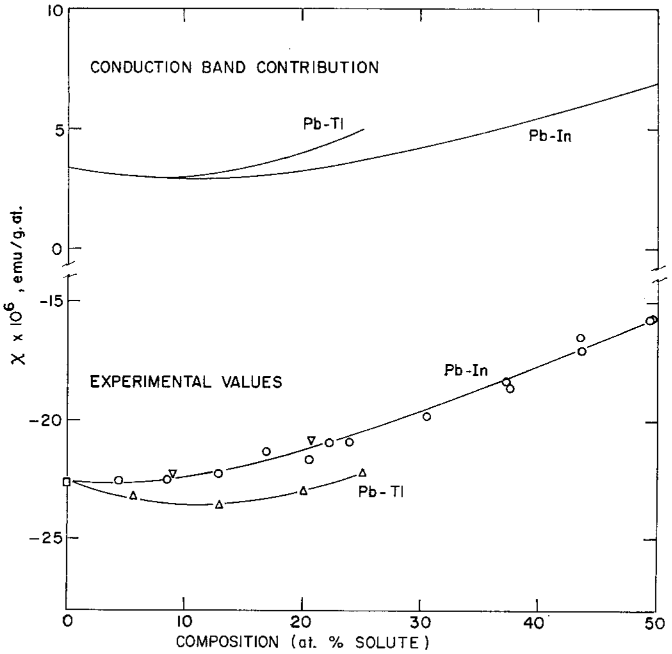

*Figure 2* Room temperature magnetic susceptibilities of lead-indium and lead-thallium alloys. Bottom curves represent directly measured experimental points, and the top curves represent the conduction band contributions which were obtained by subtracting ion core contributions from the smoothed experimental data.

the 9.0 and 20.7 at. % indium single crystals are included in the plot and are represented by inverted triangles, but no satisfactory fragment of the 5.5 at.% indium single crystal was available. The smoothed lines through the experimental points were then corrected for the diamagnetic contributions of the ion cores with the values tabulated by Selwood [12], which are $-26 \times 10^{-6}$ emu/mole for $Pb^{+4}$, $-19 \times 10^{-6}$ emu/mole for $In^{+3}$, and $-31 \times 10^{-6}$ emu/mole for $Tl^{+3}$. The resultant values are plotted in the upper portion of fig. 2 and should represent the magnetic susceptibility contributions from the conduction bands of the two alloy systems.

## 3. Discussion

It may be noted from the upper curves in fig. 2 that the susceptibility contributions from the conduction bands in the lead-thallium and lead-indium alloys are essentially the same up to ~ 7 at. % solute. Thus the data imply that at dilute solute concentrations, indium has the same effect on the electronic density of states at the Fermi level as does thallium. This leads to the inference that, at low solute concentrations, lead-indium alloys like lead-thallium alloys are well approximated by the free electron model. Above ~ 7 at. % solute the conduction band contribution to the magnetic susceptibilities of the lead-indium alloys diverges from that of the lead-thallium alloys. Since the lead-thallium alloys have already been shown to remain free-electron-like at higher solute concentrations, this must mean that the lead-indium alloys are less free-electron-like, and that a rigid band approximation becomes invalid at increased indium concentrations. Thus the band structure of lead-indium alloys is indicated to be more complex than that of lead-thallium alloys. This complication may be due to a change in the potential field within the alloys when the solute concentration becomes large enough to require indium-indium nearest neighbours. In a completely random solution solute-solute nearest neighbours must occur near 8⅓ at. % solute and the number of such neighbours must increase with increasing solute concentration. The actual divergence in the susceptibility curves begins at a slightly lower solute concentration which is to be expected in a real rather than an ideal solution, and the amount of divergence increases with increasing solute concentration. The reason for suspecting an atypical potential contribution from the indium-indium interactions is the atypical tetragonal structure of pure indium.

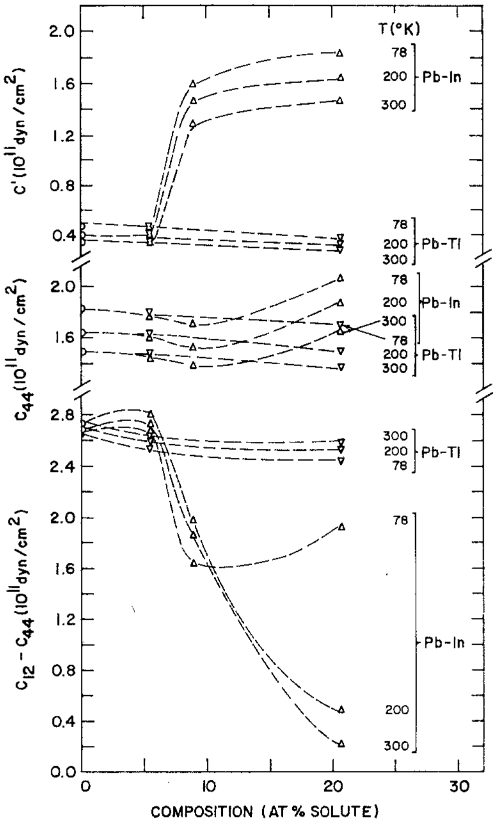

*Figure 3* Shear constants, $C_{44}$ and $C' = (C_{11} - C_{12})/2$, and electronic bulk modulus, $C_{12} - C_{44}$, for lead-indium and lead-thallium alloys at parametric temperatures.

The rigidity of a metal lattice is much more sensitive to the valence electron distribution than is the compressive resistance [13, 14]. On this basis the shear constants $C_{44}$ and $C'$ were both expected and observed to show a correlation with the magnetic susceptibility data. This is illustrated in fig. 3 where it is evident that at low solute concentrations the shear constants of the lead-thallium and lead-indium alloys are in close correspondence, but somewhere between 5.5 and 9.0 at. % solute the constants for the two alloy systems diverge. This divergence is particularly noticeable in the anisotropy ratios, $2C_{44}/(C_{11}-C_{12})$, which for the lead-thallium alloys and the 5.5 at. % lead-indium alloy are found to be close to the anisotropy ratio of pure lead with values near 4. In contrast, both the 9.0 and 20.7 at. % lead-indium alloys have anisotropy ratios near unity (see fig. 4). Thus there is additional evidence that in the lead-indium alloys a signifi-

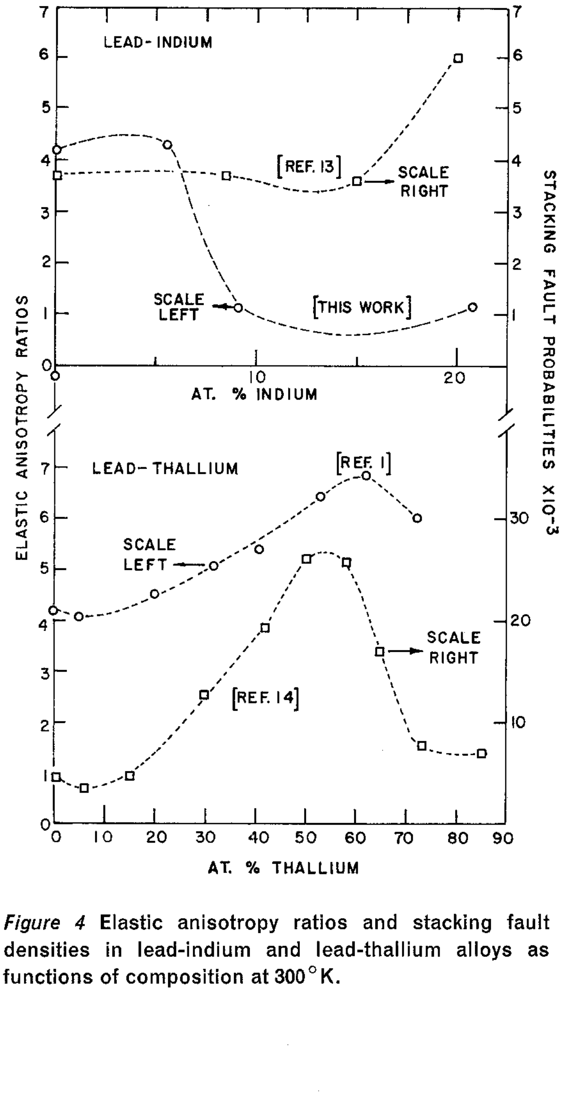

*Figure 4* Elastic anisotropy ratios and stacking fault densities in lead-indium and lead-thallium alloys as functions of composition at 300°K.

cant change occurs between 5.5 and 9.0 at. % indium. This is attributable to that portion of the shear resistance which is sensitive to the details of the electronic occupancy of the valence bands, because the mathematical form of the other contributions to the anisotropy ratio indicate that these other contributions should vary smoothly across the phase field. Corroboration that the change is electronic in origin is furnished by the bottom curves in fig. 3, which show $(C_{12}\text{-}C_{44})$ for the lead-indium and lead-thallium alloys at different temperatures. For cubic materials $(C_{12}\text{-}C_{44})$ is a measure of the degree of deviation from the Cauchy relation, and de Launay [15] has shown that this quantity is in the nearly-free-electron limit the bulk modulus of the electron gas. In fig. 3, the initially faster rise of $(C_{12}\text{-}C_{44})$ for lead-indium alloys over $(C_{12}\text{-}C_{44})$ for lead-thallium alloys is primarily a reflection of the greater spatial density of the "free-electron gas" in the lead-indium alloys. However, the sharp downward trend of $(C_{12}\text{-}C_{44})$ between 5.5 and 9.0 at. % indium in the lead-indium alloys is consistent with the behaviour of $C_{44}$ and $C'$ and must reflect a pronounced change in the energy distribution of the valence electrons in wave-number space. Subtraction of the electronic bulk modulus $(C_{12}\text{-}C_{44})$, from the normal bulk modulus, $\frac{1}{3}(C_{11}+2C_{12})$, yields a quantity which may simplistically be called the lattice bulk modulus and this quantity for all three of the lead-indium single crystals shows a normal decrease with increasing temperature.

In both the lead-indium and lead-thallium systems there is a qualitative correlation between the compositional dependence of the anisotropy ratios and the stacking fault densities. This is shown in fig. 4 where the compositional dependencies of the stacking fault densities have been taken from studies [16, 17] of peak shifts in X-ray diffraction patterns. Within the resolution of the data it appears that the two properties vary nearly in phase. This is true in the sense that at any given composition the slopes of the compositional dependence of both properties tend to have the same sign, and maxima and minima occur for both properties in the same composition regions. Certainly the quantitative relations between elastic constants, dislocation densities, and stacking fault parameters are complex [18-20]. Nonetheless, the calculations of Teutonico [21] have shown that an increasing degree of elastic anisotropy favours an increased splitting of dislocations to form wider stacking faults, and the observed behaviour is consistent with this predicted trend.

## Acknowledgements

The authors wish to thank Drs G. W. Shannette, T. Prevender, and J. Tonnies for assistance with the experimental techniques and apparatus. Gratitude is also due to Dr C. V. Banks for the chemical analyses, to Mr Dean Dietz for preparation and measurement of some of the lead-indium susceptibility samples, and to Mr F. Laabs for performing the microprobe analyses. The financial support of one of the investigators (J. v. d. P.) by the National Fonds voor Wetenschappelijk Onderzoek is also gratefully acknowledged.

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Received 17 May 1971 and accepted 5 July 1971