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SUMMARY

The dynamic Young's modulus - composition relation in eutectic alloy systems, without terminal solid solubility, follows either a linear relation or a less than linear relation. Essentially linear relations are obtained for systems where the moduli differences between the two phases are small or when the microstructure of the alloy exhibits a strong fibered texture such as is obtained in a cold drawn material. Eutectic systems containing a random distribution of phases with large moduli differences between the phases exhibit less than linear relations between modulus and composition. The theory of Hashin and Shtrikman is in qualitative agreement with experimental data obtained in the Ag-Pb system. Quantitatively, the actual modulus values of the composite are higher than the predicted values. This discrepancy may be due to the presence of internal stresses at the Ag-Pb interface which factor is not taken into consideration in the Hashin-Shtrikman theory.

INTRODUCTION

KOSTER AND RAUSCHER (1948) were among the first to investigate systematically the influence of composition on the dynamic Young's modulus, E, of several binary eutectic systems. It would appear that in a large number of cases the correlation between modulus and composition is a linear one. For example, linear relations were observed in the Al-Zn, Cu-Ag, Pb-Sb, Pb-LiPb and Bi-LiBi systems. On the other hand, relations that were less than linear were observed in systems such as Pb-Sn, Al-Si and Cu-Cr. It is therefore clearly evident that different trends in the modulus - composition curves exist. The linear relations observed by Koster and Rauscher are particularly disturbing inasmuch as several contemporary theories of elasticity of composite bodies [B. PAUL (1960), Z. HASHIN AND S. SHTRIKMAN (1963), R. HILL (1963), and TAI-TE WU (1964)] generally predict a non-linear (below linear) relation between Young's modulus and composition in two-phase composites such as is present in binary eutectic systems.

It was thought that a thorough evaluation of the elastic modulus of a typical eutectic, wherein the two components differed widely in their modulus values, would shed some light on the observed discrepancies. The system Ag-Pb was chosen for study since the modulus of silver is about four times higher than the modulus of lead at room temperature. An evaluation of the temperature dependence of modulus in this system could also prove useful since the ratio E_{Ag} to E_{Pb} increases with increasing temperature and is over five near the melting point of lead. Another factor favoring a study of this system is that the two elements are virtually insoluble in each other and complications arising from solid solution alloying and solubility changes with temperature are minimized. The lead-silver phase diagram as adapted from HANSEN (1958) is shown in Fig. 1. With the exception of a single Ag-Pb alloy investigated by KOSTER AND BANGERT (1951) the only previous study on elastic properties of Ag-Pb alloys appears to have been done by UMEKAWA (1955). The results of this investigation revealed a nearly linear relation between composition and modulus (Fig. 6). The alloys measured by Umekawa, however, were prepared by cold drawing cast ingots into wires (80% reduction in area) and it is possible that the strong fibered texture developed may have contributed to the nearly linear relation observed.

MATERIALS AND EXPERIMENTAL PROCEDURE

Silver-lead alloys were prepared at increments of about ten volume percent in composition. Mixtures of 99.95% pure silver and 99.99% pure lead were prepared in 70 gram batches. They were melted in a ceramic crucible covered with charcoal to minimize oxidation. Casting temperatures were about 100°C above the liquidus line and the alloys were then poured into metal molds 1/4" in diameter and 5" in length. Specimens were machined directly from the cast ingot into circular rods typically 0.2" in diameter and 4" in length. Specimens were then annealed directly below the eutectic temperature (304°C) to minimize casting stresses. Some typical microstructures are shown in Fig. 2. The microstructural distribution of phases was generally homogeneous and the castings appeared relatively free of shrinkage cavities. The density of the samples tested is shown in Fig. 3. The small deviation from a linear correlation attests to the high density of the Ag-Pb specimens evaluated. All correlations with composition are given in volume fraction (or percent) of one of the two phases present.

The dynamic modulus was measured by inducing a both-end-free trans-

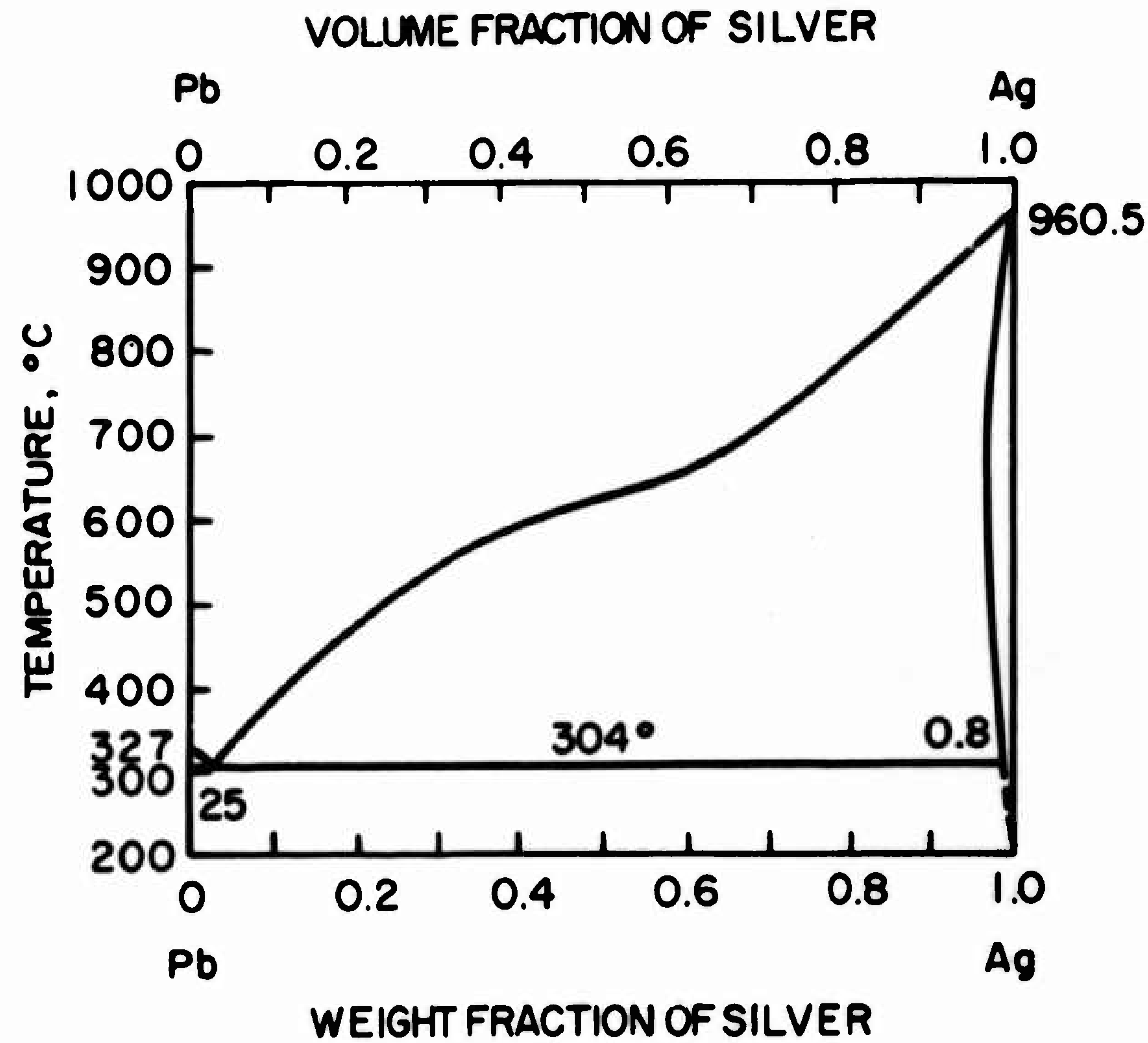

Fig. 1. Equilibrium phase diagram for the lead-silver system (adapted from Hansen 1958).

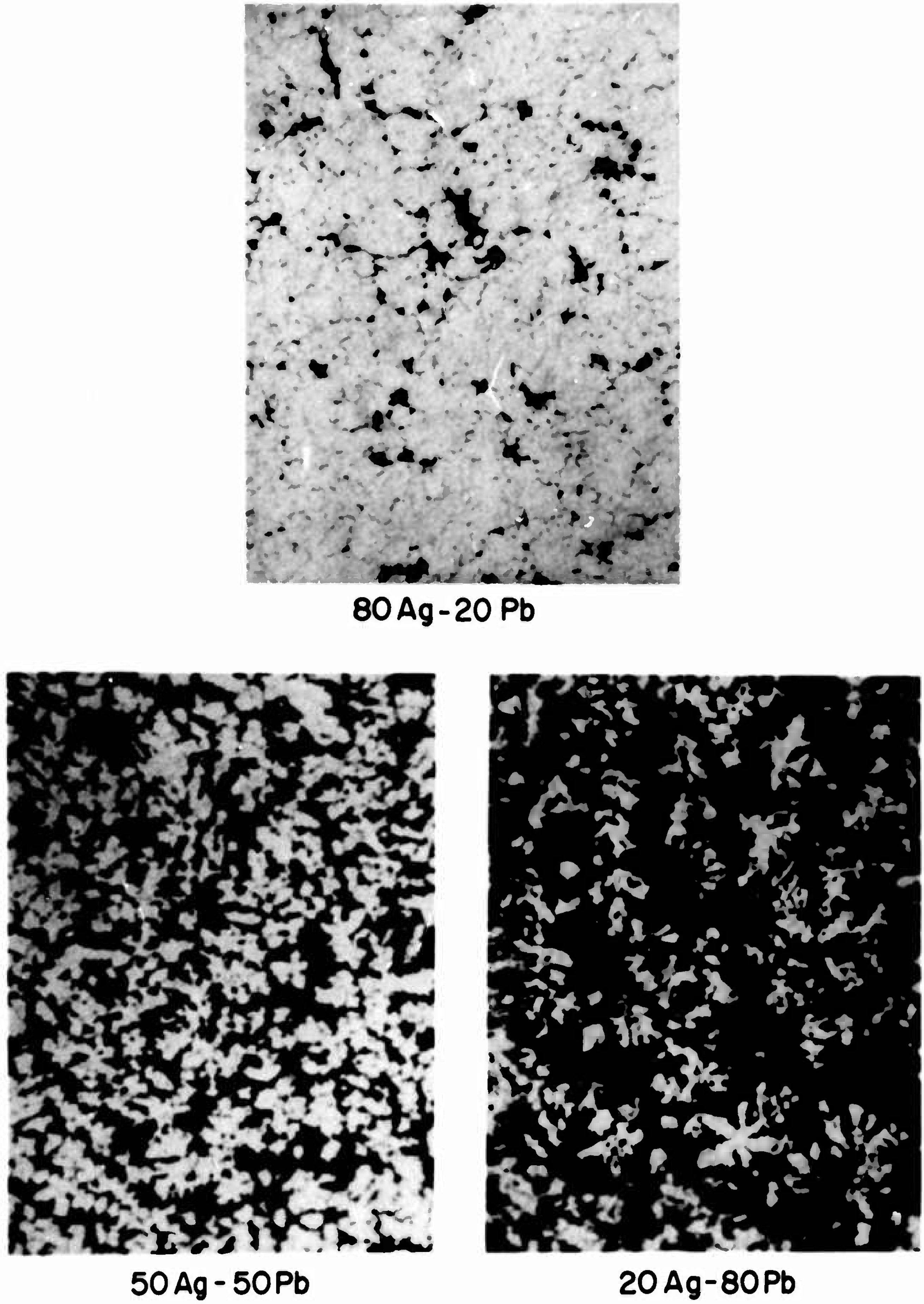

Fig. 2. Photomicrograph of cast silver-lead alloys (500-X).

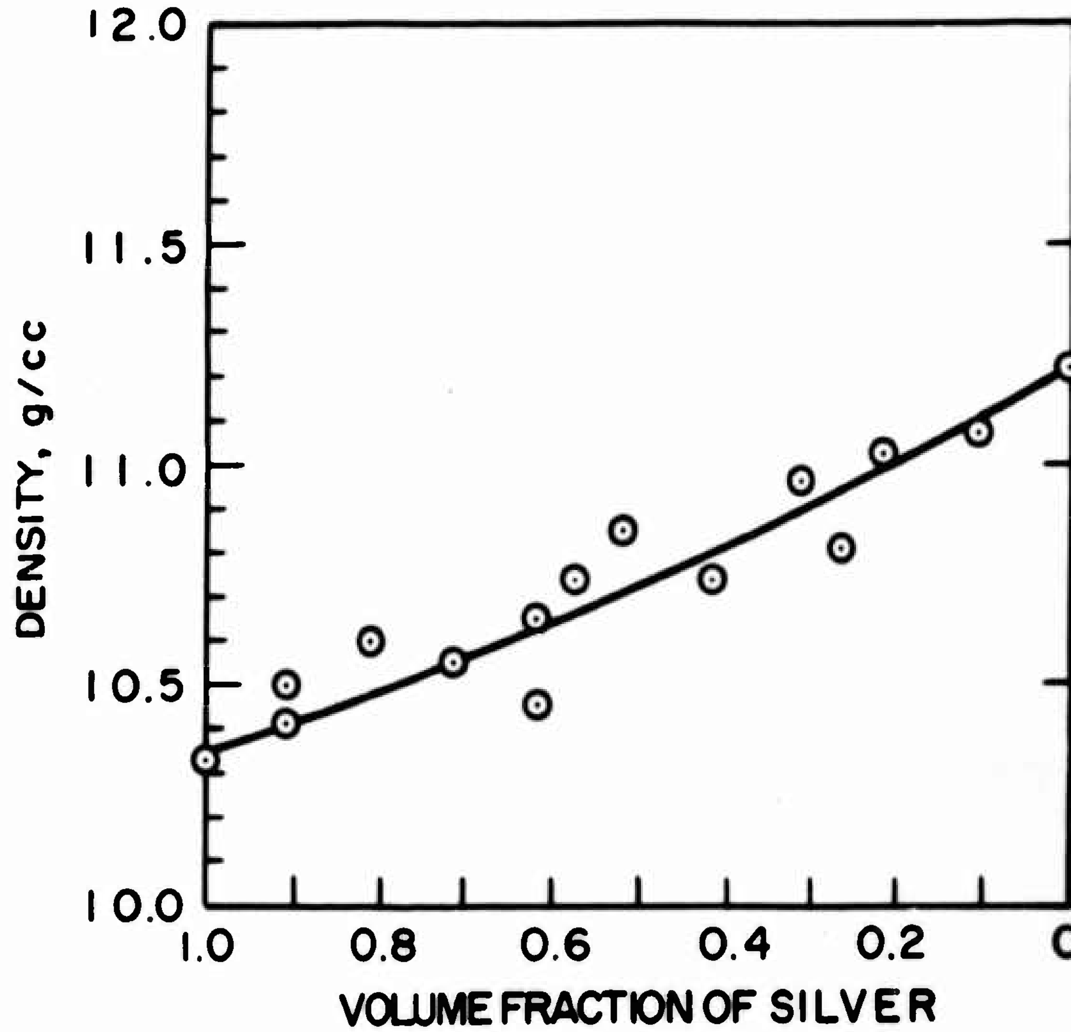

Fig. 3. Relationship between density and volume fraction of silver in cast silver-lead alloys.

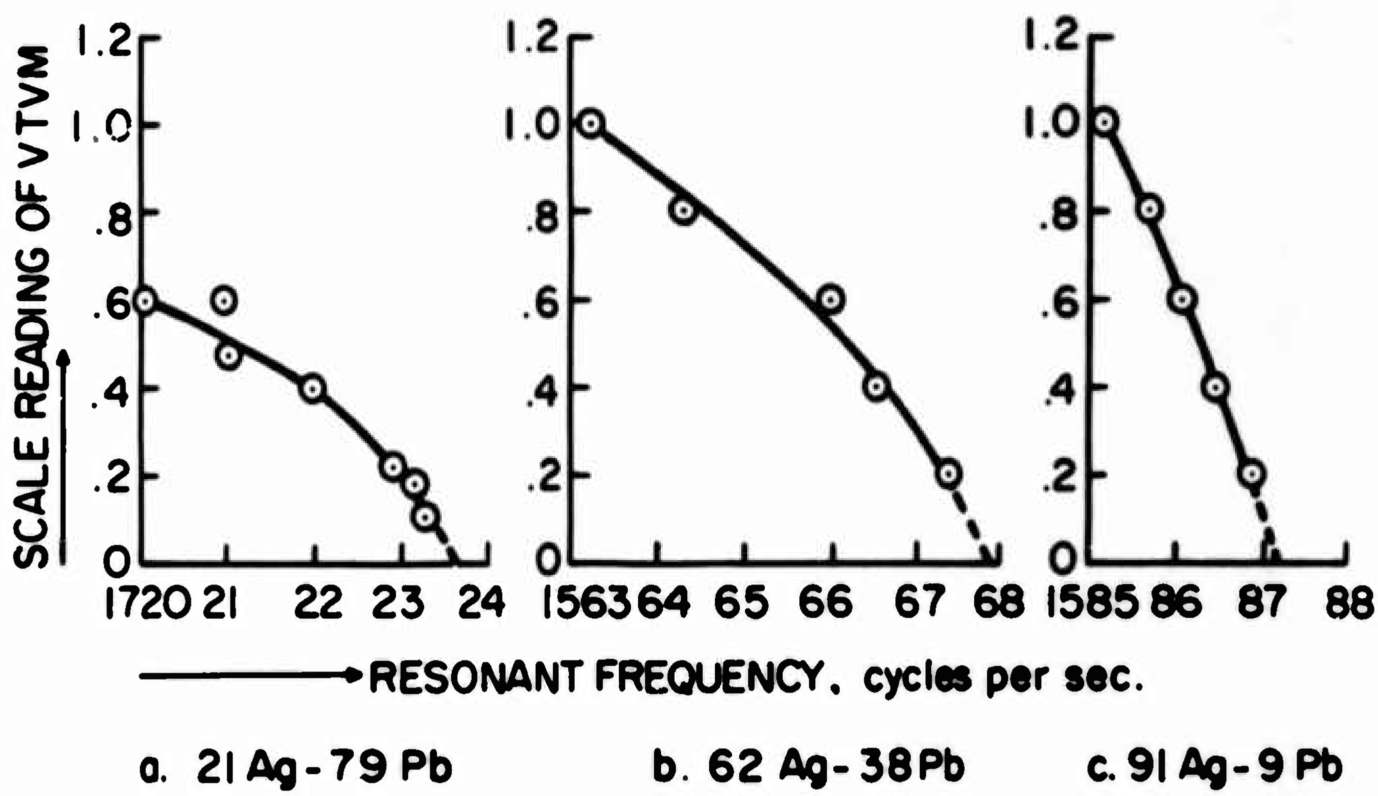

Fig. 4. Examples illustrating the relationship between resonant frequency and strain amplitude in three silver-lead alloys.

verse vibration on the samples. The method of testing is similar to that described in another paper (J. L. LYTTON ET AL, 1964) and will therefore not be detailed here. Elevated temperature tests were performed by heating the specimens in an elliptical furnace. The heating source was a quartz lamp held at one focal point of the furnace and the specimen was supported by driving and sensing wires at the other focal point. Alumel was used as a driving wire and mechanical vibrations were induced into the wire by means of an earphone. The principal advantage of an earphone over a loudspeaker is that no self-resonant peaks can be detected in such a device up to a frequency of 5000 cycles per second. The response of the specimen to mechanical vibrations was detected through a chromel support wire to a Rochelle salt phonograph pickup. The chromel-alumel support wires also served as a thermocouple with the specimen as the junction. Specimen temperatures were measured within an accuracy of $\pm$ 2°C.

Since lead yields plastically at low stresses, it was necessary to measure the resonant frequency at very low strain amplitudes in order to minimize plastic and anelastic strain effects. The resonant frequency of samples through which Young's modulus was calculated was obtained by extrapolation of the resonant frequency to zero amplitude. An example of the amplitude dependence of the resonant frequency of several Ag-Pb alloys is shown in Figure 4.

A detailed description of the apparatus and the variables involved in dynamic modulus measurements is given in the Appendix.

RESULTS

The influence of composition on the dynamic Young's modulus of Ag-Pb alloys at room temperature is given in Fig. 5. As can be seen the relation is considerably below a linear one. In contrast, the results on

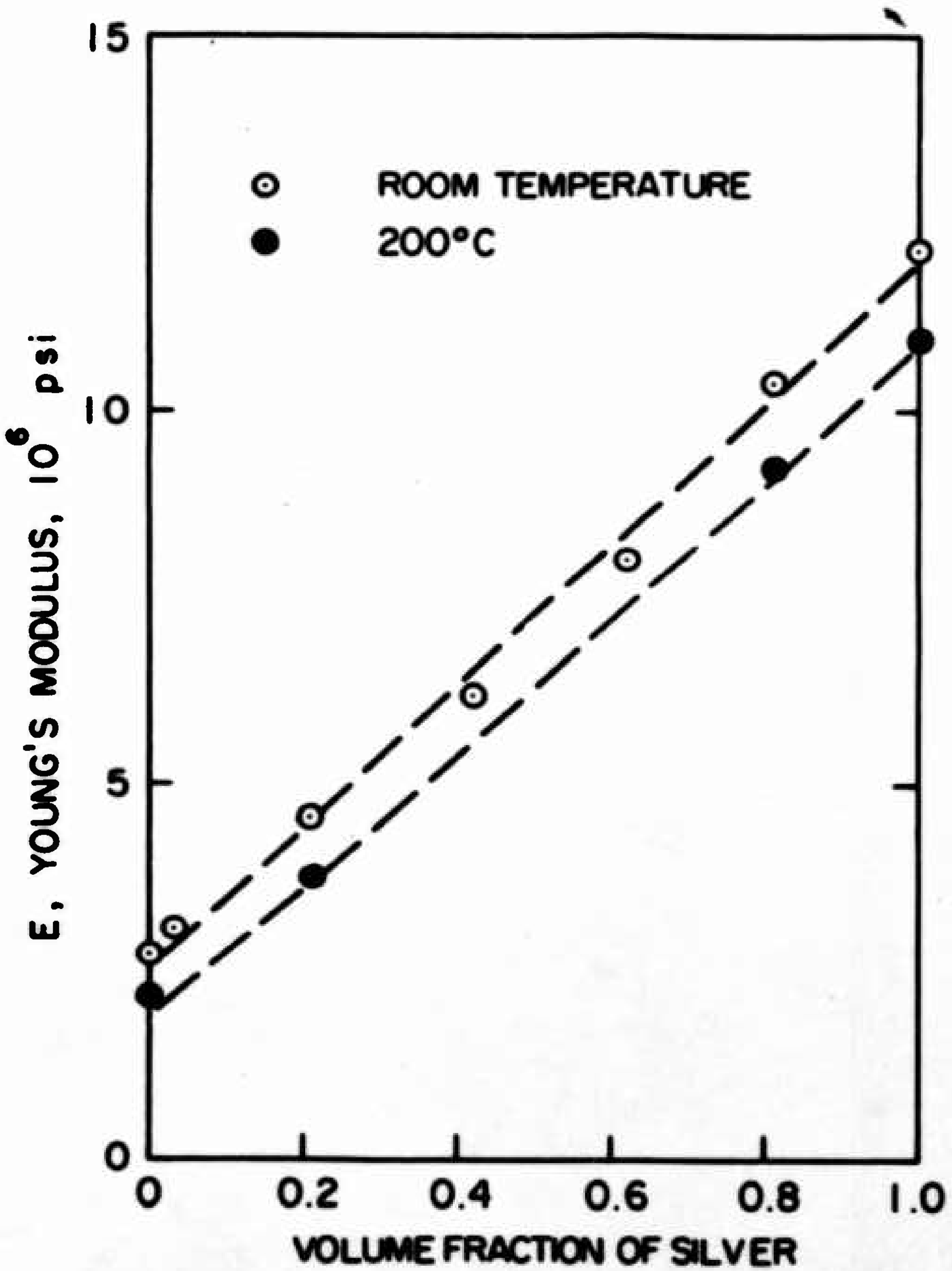

Fig. 5. Relationship between Young's modulus and composition in highly oriented silver-lead alloys (obtained by cold drawing). Data of UMEKAWA, 1955.

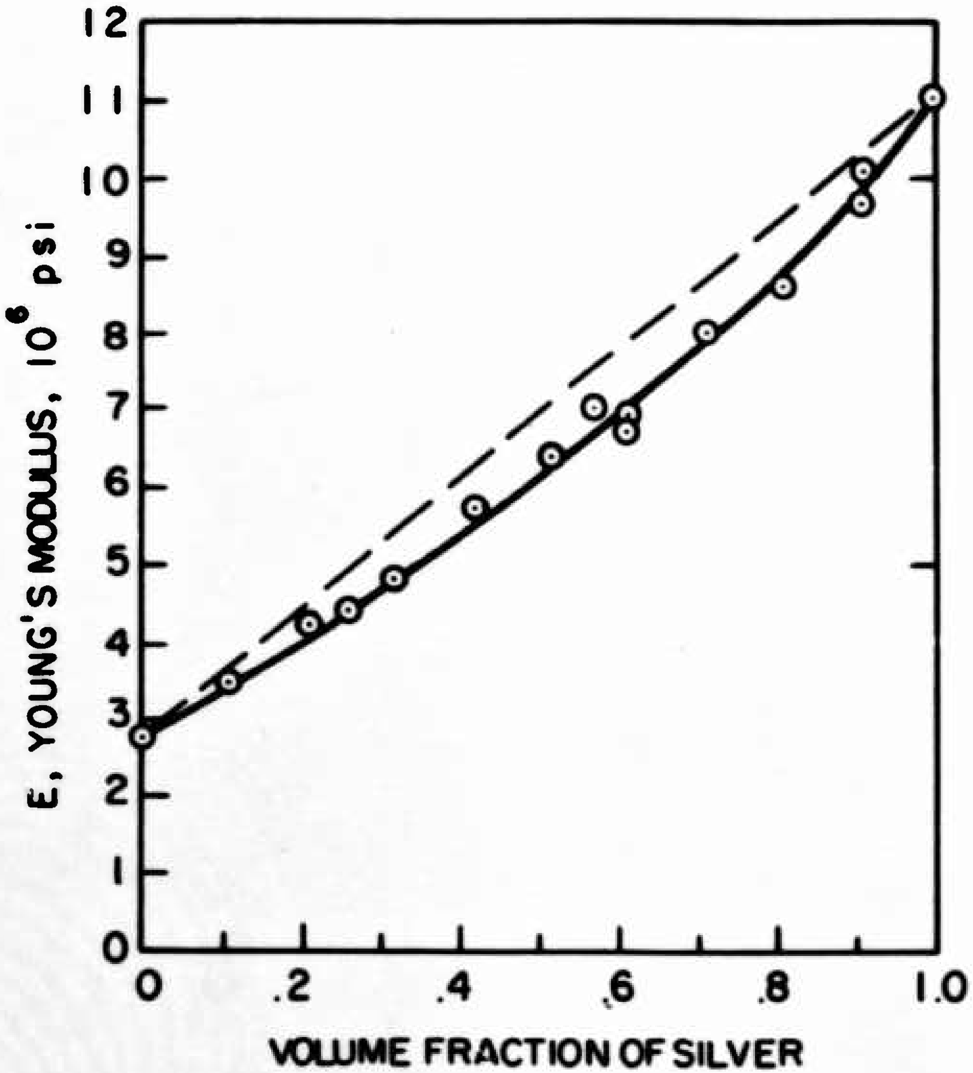

Fig. 6. Relationship between Young's modulus and composition in cast silver-lead alloys at room temperature.

heavily cold-drawn wires performed by one of the authors (S. UMEKAWA, 1955) is given in Fig. 6. These latter alloys exhibited a nearly linear correlation between the dynamic Young's modulus and composition. The moduli of these cold drawn alloys were measured in the direction of working.

Modulus-temperature relations for several of the cast Ag-Pb alloys were determined and the results obtained are graphically illustrated in Fig. 7. Measurements on the alloys were taken up to the eutectic temperature. The specimens would quite often break in a brittle manner if tested above the eutectic temperature although it was possible in at least one sample (91 Ag- 9 Pb alloy) to measure a modulus value above the eutectic temperature. A discontinuity in the modulus was observed in this case wherein the modulus of the Ag-Pb alloy was reduced by about 5% upon melting of the eutectic regions.

DISCUSSION

A comparison of Figures 5 and 6 reveals the importance of considering the morphology of the structure in determining the modulus - composition relation. The cold-drawn samples tested (Fig. 6) exhibited an oriented structure of the two phases and the relation between modulus and composition in this case tends to be almost linear. This is in agreement with the theory proposed by PAUL (1960) for oriented structures. This theory assumes that both phases are experiencing the same strain under a given stress (isostrain theory) which leads directly to a linear relation between the modulus and the volume percent of second phase. Copper samples containing tungsten fibers when tested in the direction of fibering (McDANELS, JECH AND WEETON, 1963) also reveal a linear relation between the dynamic Young's modulus and composition.

The alloys containing random distributions of silver and lead ex-

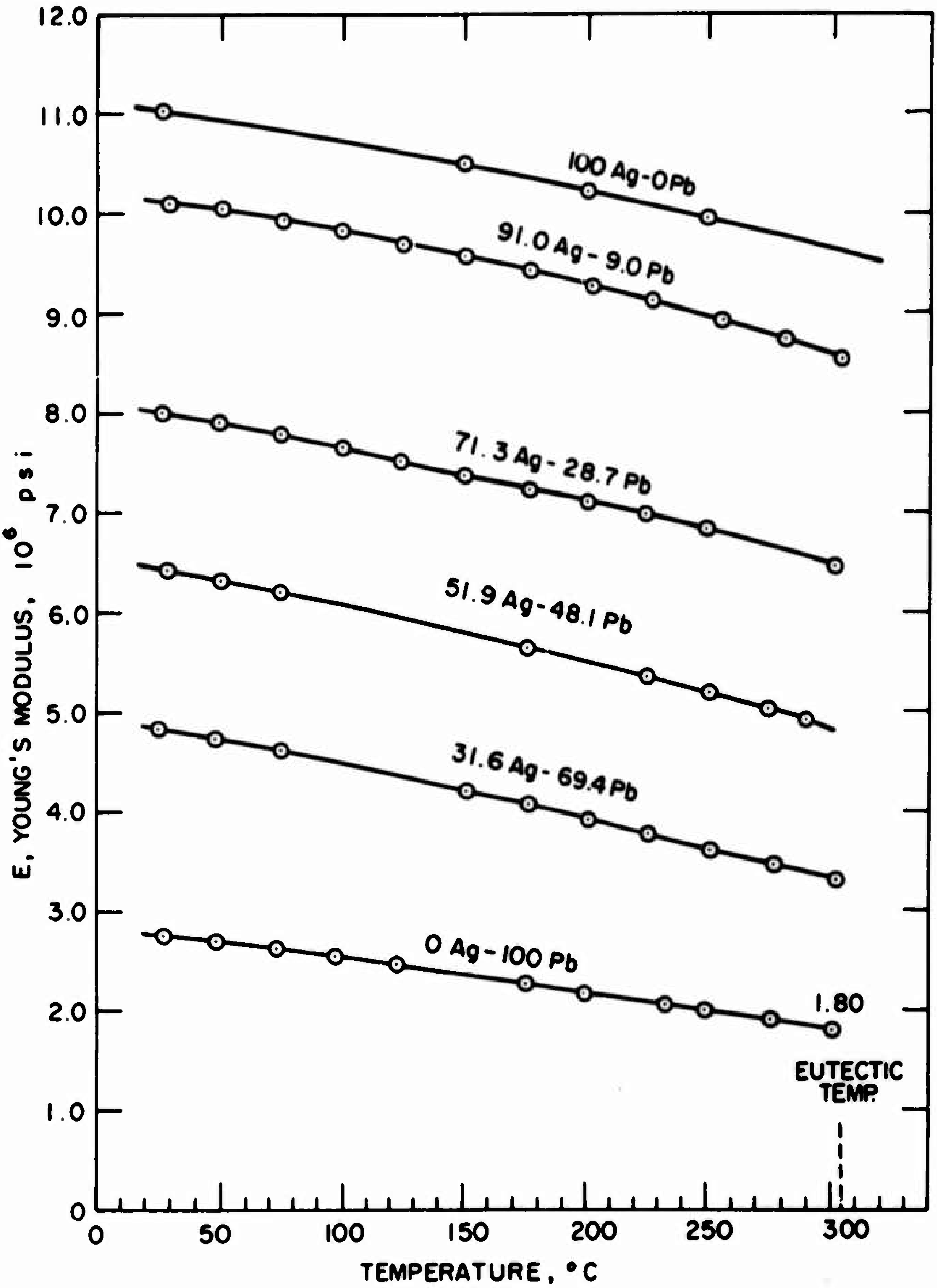

Fig. 7. Relation between Young's modulus and temperature in silver-lead alloys.

hibit a less than linear relation (Fig. 5). This observation is in qualitative agreement with the theoretical predictions of HASHIN AND SHTRIKMAN (1963). A quantitative comparison of the Hashin-Shtrikman theory with experimental data requires a knowledge of Poisson's ratio, ν. A value of $\nu = 0.38$ was chosen for silver and $\nu = 0.45$ for lead (KOSTER AND FRANZ, 1961). Using these values for Poisson's ratio, the bulk and shear modulus of pure silver and lead can be determined. The bulk and shear moduli of the composite are then evaluated by the equations developed by Hashin and Shtrikman. Young's modulus for the composite is calculated from the equation relating E, G and K, namely $E = \frac{9\,K\,G}{3K + G}$. Figure 8 reveals the upper and lower bounds predicted by the theory of Hashin and Shtrikman for K, G and E. The theoretical curves for E are compared with the experimentally determined values for Young's modulus in the same figure. As can be readily seen the experimental points fall very close to the upper bound curve of the Hashin-Shtrikman theory.

At this point one may wish to consider how good the theory of Hashin-Shtrikman is for the typical eutectic system chosen for study. The upper bound is based on the presence of a continuous matrix of the hard phase with the soft phase distributed discontinuously within the matrix. The lower bound theory assumes that the matrix material is the soft phase with the hard phase discontinuous. The phase diagram for the Ag-Pb system is such that almost all alloys crystallizing from the melt first have proeutectic silver colonies forming (since the eutectic composition is so near to pure lead) and then, at the eutectic temperature, the lead and silver phases precipitate out simultaneously. Since the eutectic consists mostly of pure lead it is reasonable to assume that the eutectic structure consists of a continuous sea of lead

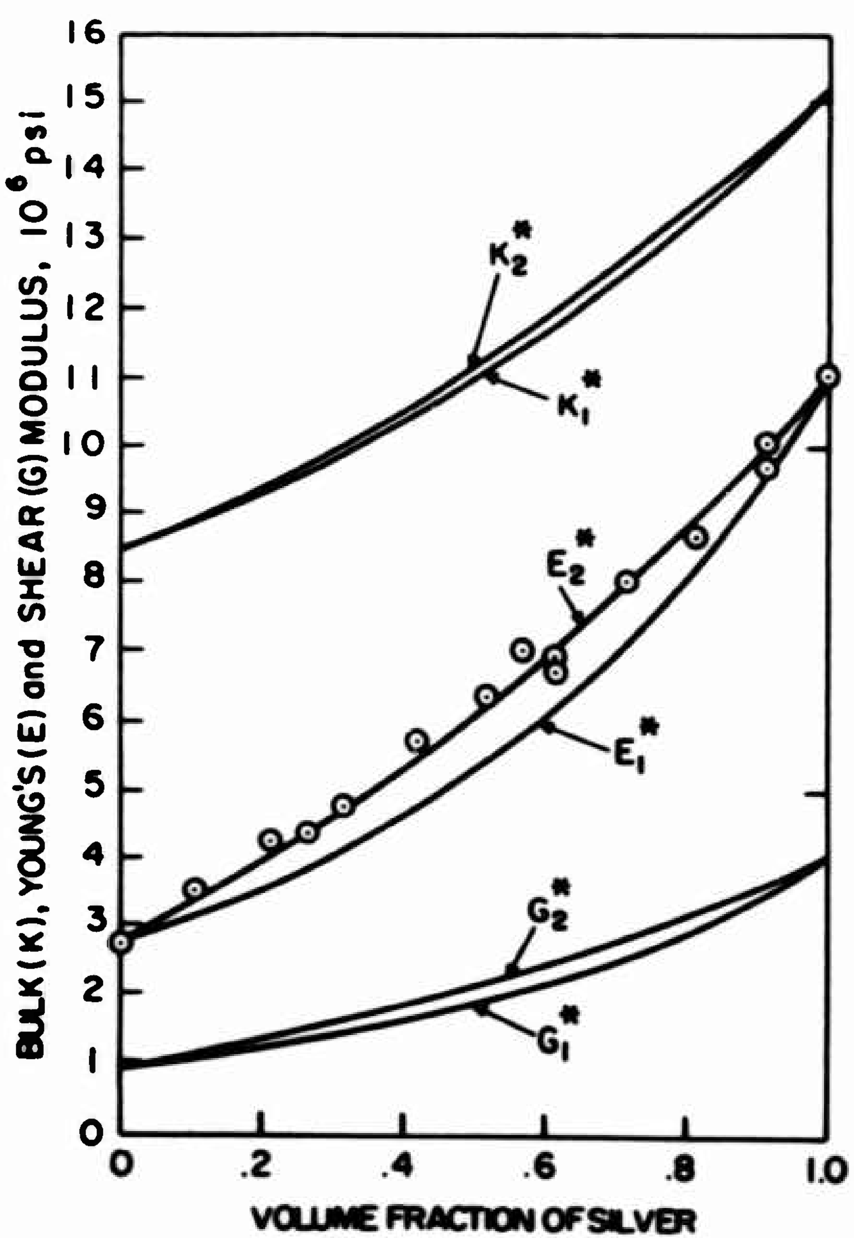

Fig. 8. Comparison of the dynamic Young's modulus-composition data for cast silver-lead alloys with the upper and lower bound predictions of the Hashin-Shtrikman theory.

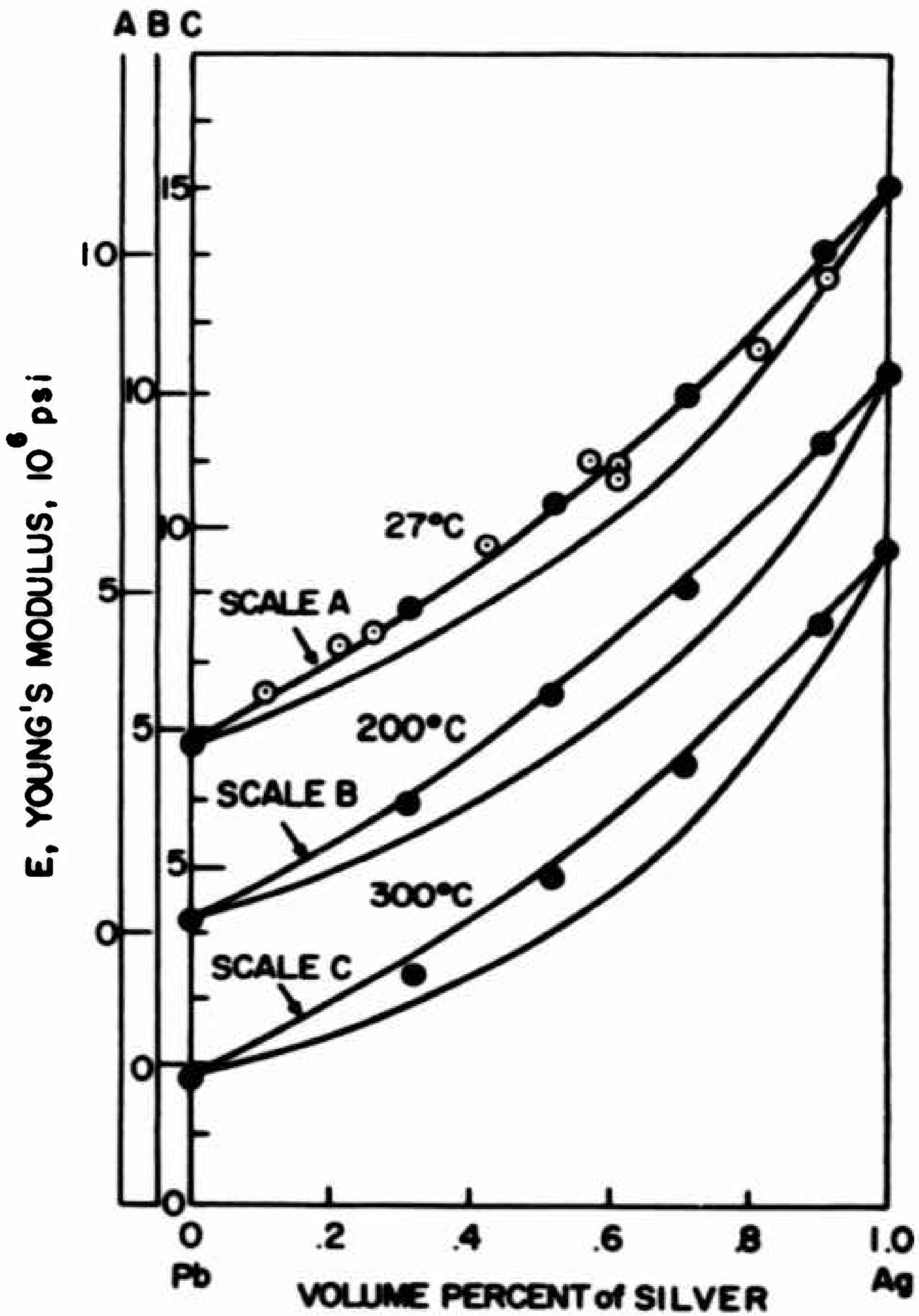

Fig. 9. Comparison of the dynamic Young's modulus-composition data for cast silver-lead alloys with the upper and lower bound predictions of the Hashin-Shtrikman theory at various temperatures.

with a fine dispersion of discontinuous silver particles. The structure of the eutectic (black regions shown in Fig. 2) is so fine that it was not possible to confirm this hypothesis even when viewed at high magnification (1000X). Electron metallography on the samples tested did not help to clarify the distribution of phases in the eutectic. Because the silver precipitates out first and the eutectic last in most of the alloys studied, it might be reasonable to assume that the eutectic forms the continuous structure. Under this assumption the elastic modulus - composition curve might be expected to correlate with the lower bound curve of the Hashin-Shtrikman theory. On the other hand, if the distribution of the two phases is random, then the mean value of the upper and lower bounds of the theory should be applicable. From either viewpoint, a clear discrepancy exists between the experimental data and the Hashin-Shtrikman theory. This difference (about 5 to 15% at the 50-50 composition) may be explained on the basis that an internal stress exists at the interface of the silver-lead phase regions. These internal stresses can arise at the time of formation of the structures at the eutectic temperature. Additional stresses can be created from the difference in thermal expansion coefficients of lead and silver. After the eutectic is formed at 304°C, the lead phase contracts upon cooling at a rate which is about twice as fast as the silver phase. This factor could lead to a tensile stress in the lead phase and a compressive stress in the silver phase. Such internal stresses are not taken into account in the Hashin-Shtrikman theory. Internal stresses are likely to exist in all binary eutectic alloy systems since the two phases would be expected to wet (bond) and would probably be coherent with each other at all interfaces. Similarly, in non-eutectic, two-phase systems such as WC-Co, W-Ag or W-Cu, the two phases would be also expected to wet at the interface and coherency stresses could develop at such interfaces as well. It is therefore not entirely clear why a nearly perfect correlation was obtained between the experimental data of NISHIMATSU AND GURLAND (1960) on WC-Co alloys and the theory of HASHIN AND SHTRIKMAN (1963). Further experimental and theoretical studies are necessary to elucidate the possible influence of wettability and coherency stresses on elastic properties of two-phase composite materials.

The modulus - composition relation for Ag-Pb alloys at various temperatures is given in Figure 9. As can be seen the influence of temperature is to shift the experimental data downward in relation to the theoretically predicted curves. At 300°C the data fall in between the upper and lower bounds of the Hashin-Shtrikman theory. One possible explanation for this trend is that the theory is more nearly applicable to describing the elastic properties of eutectic systems at high temperature where the internal stress between the phases present may be somewhat reduced. Another explanation is possible, however, based on the influence of interphase boundary shearing on elastic properties at high temperatures. Such a shearing phenomenon could contribute to a decrease in modulus similar to the drop in modulus observed in grain boundary shearing (C. ZENER, 1948). A relaxation phenomenon of this type should contribute to a high damping capacity. This was, in fact, observed to be the case in an Ag-Pb specimen (89Ag-11Pb) studied by Koster and Bangert. These investigators found that the damping capacity of the sample was higher below the eutectic temperature than above the eutectic temperature. The decreased value of damping capacity above 304°C might be expected since the liquid metal is relatively free to shear past the silver boundary regions. A similar modulus relaxation was observed in a W-Ag composite by UMEKAWA, KOTFILA AND SHERBY (1964) at temperatures approaching the melting temperature of silver.

The question can now be asked as to why some eutectic systems exhibit linear relations between the modulus and composition whereas others exhibit curvilinear relations. It is believed that the major reason why nearly linear relations were observed by Koster and Rauscher in the Al-Zn, Cu-Ag, Pb-LiPb, Bi-LiBi systems was because the modulus differences of the phases were small. The modulus ratio varied from 1.3 to 1.9 in these systems. Under these conditions the Hashin-Shtrikman theory would predict a nearly linear correlation and therefore there is no discrepancy to consider. An example of such a system is the Cd-Bi system. The modulus-composition data for this system (S. UMEKAWA, UNPUBLISHED REPORT) are compared with the theoretical prediction of Hashin and Shtrikman in Figure 10. The upper and lower bounds for the theory superimpose and deviate only slightly from a linear relation. The experimental data, similarly, exhibit a nearly linear relation. In other cases, however, the moduli of the two phases differ appreciably and there is still a linear relation (e. g., the Pb-Sb system studied by Koster and Rauscher where $\frac{E_{Sb}}{E_{Pb}} = 2.8$). It is believed that this result is due to the presence of a strong texturing in the composite. Young's modulus measurements made in the direction of texturing would be expected to show a nearly linear relation in agreement with the isostrain theory of Paul. This suggestion is borne out for the case of the Ag-Pb alloys discussed in this investigation. As mentioned previously, the textured samples obtained by cold-drawing exhibit a nearly linear relation (Fig. 6) whereas the cast samples

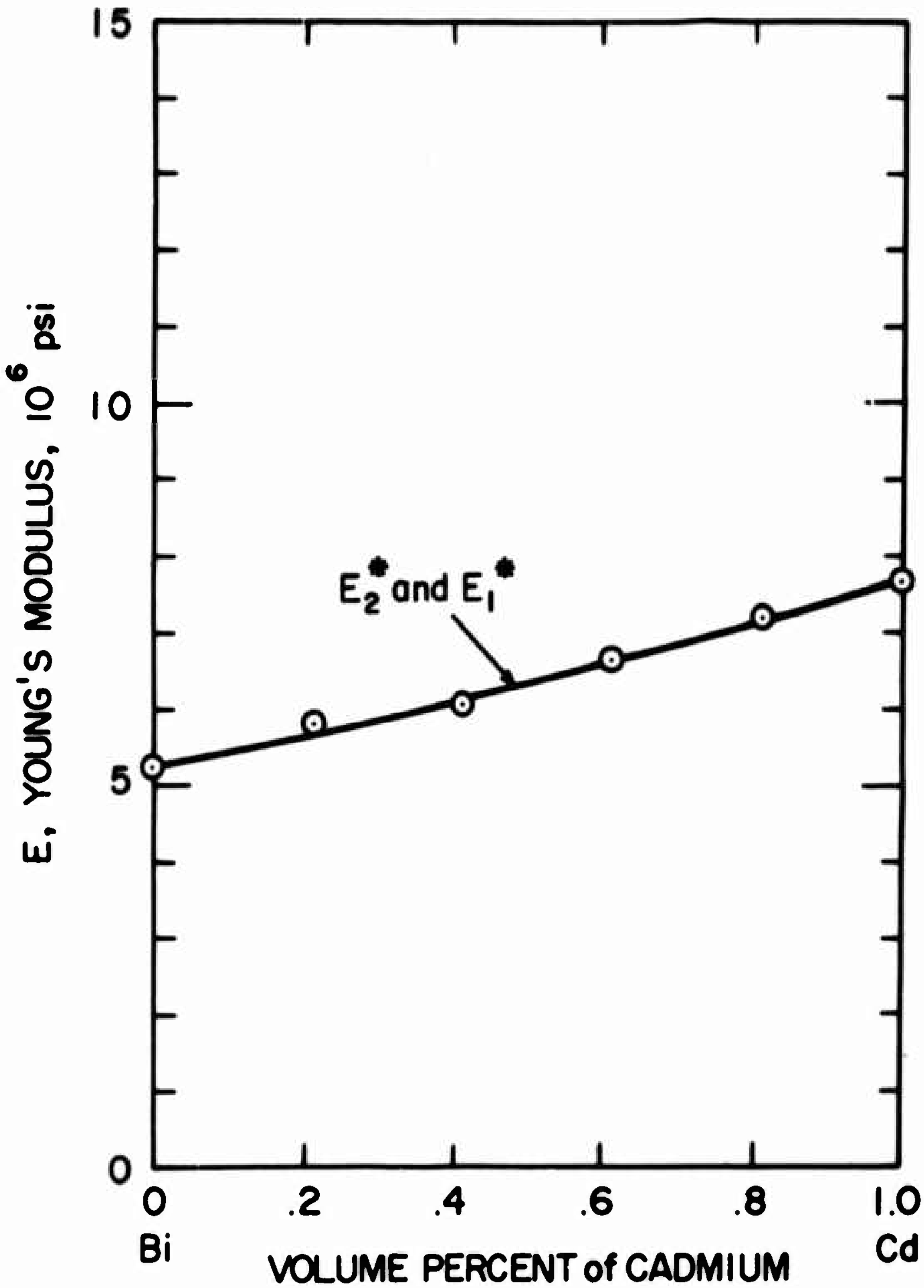

Fig. 10. Comparison of the dynamic Young's modulus - composition data for cast bismuth - cadmium alloys with the predictions of the Hashin-Shtrikman theory.

exhibit a curvilinear relation (Fig. 5).

ACKNOWLEDGMENTS

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APPENDIX

EXPERIMENTAL PROCEDURE FOR DYNAMIC MODULUS MEASUREMENTS OF SILVER-LEAD ALLOYS

The principle of the measurement is based on the both-end-free vibration. A schematic diagram of the apparatus is illustrated in Fig. A1. To measure Young's modulus at elevated temperature, the specimen is put in the focal line f_1 of a cylindrical reflectance furnace in the shape of an ellipsoidal cross-section. The heating element, in the form of a quartz lamp, is placed on the other focal line f_2. The thin alumel and chromel wires, which are connected to the driver and detector of vibration respectively, are attached to the specimen and provide the temperature measuring device. The test setup is similar to that of the apparatus described elsewhere (J. L. Lytton, et al., Brit. J. Appl. Phys., 1964, 15, 1573), although the vibrational system was modified in this study. Mechanical vibrations on the test specimen were induced by means of an earphone, the principal advantage being that no resonant peaks can be detected in such a device within the frequency range up to 5000 cycles per second. The vibration of specimen is detected by a Rochelle salt phonographic pickup, the frequency response of which also does not have any peak up to 5000 cycles per second. Output of the detector is connected to a vacuum tube voltmeter (VTVM) and cathode-ray oscillograph (oscilloscope) through a pre-amplifier of 20 - 40 db. Output of the oscillator is connected to a frequency counter.

In most cases, the fundamental frequency of specimens was measured with the specimen supported at its nodal points. The size of the wires was generally 0.005" in diameter and 0.5" - 10" in length, although in some cases thicker wires were used depending on the vibrational conditions.

As is well known, the resonant frequency of a straight bar with uniform cross-section in lateral vibration is related to the modulus by the following equation:

$$f = \frac{m^2}{2\pi L^2}\sqrt{\frac{EIg}{\rho A}} \qquad (1)^*$$

* This equation gives sufficiently accurate values of E when the bar has a small cross-sectional area compared to the length.

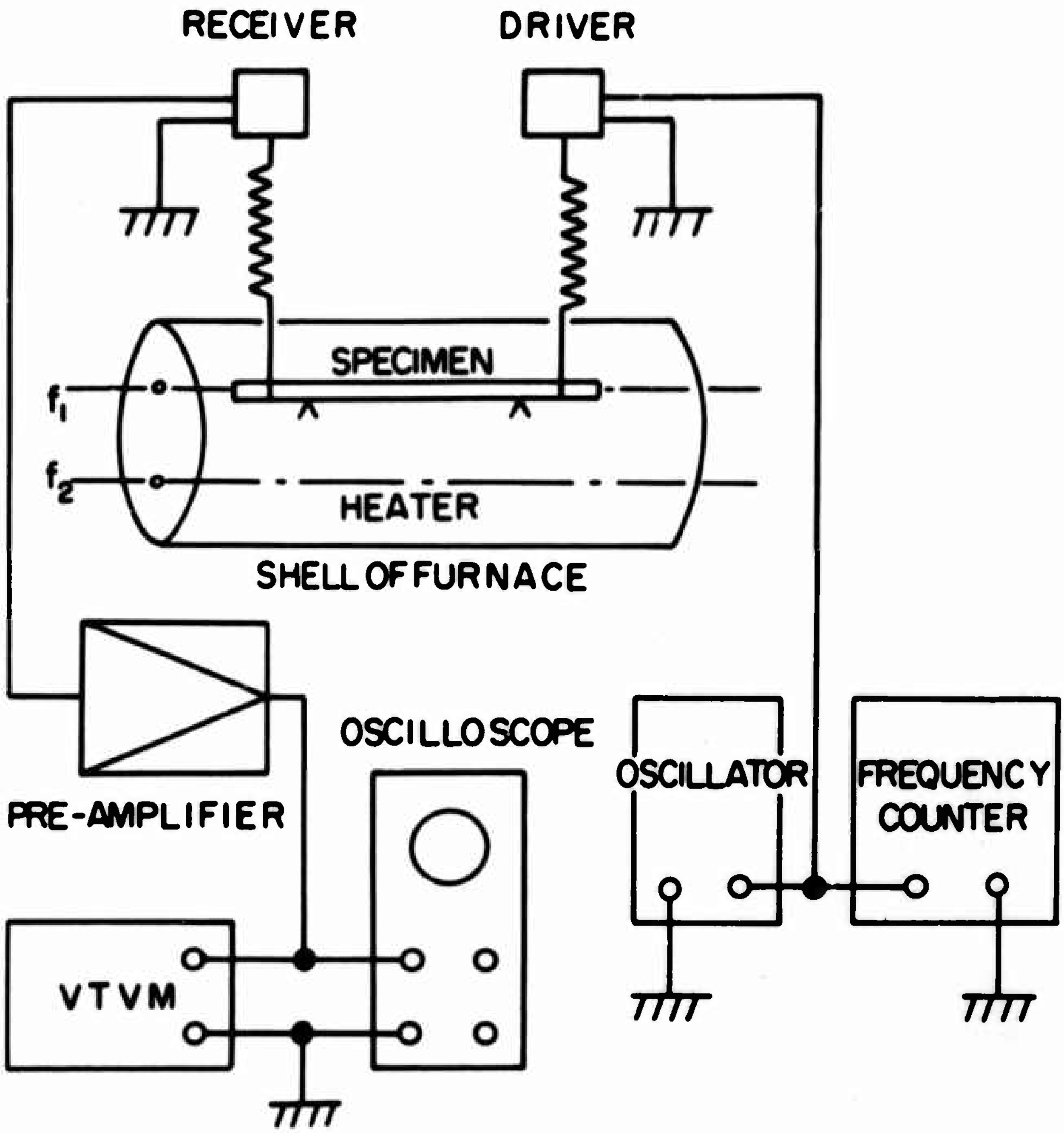

Fig. A1. Schematic diagram of aoparatus.

where f is the resonant frequency, L is the length, E is the Young's modulus, I is the moment of inertia, A is the cross-sectional area, ρ is the density, g is the gravity constant, and m is the non-dimensional constant determined by the mode of vibration as follows:

mode or harmonic	1st	2nd	3rd
m	4.730	7.853	10.996

Each variable in Equation (1) can be easily obtained with an accuracy of higher than the order of 0.1%. The resonant frequency, however, is sometimes measured with less accuracy because of several mechanical effects as follows:

(a) The effect of the position at which the wires are connected to the specimen.

The amplitude as a function of position is calculated by the following equation:

$$Z = \frac{Z(\ell)}{2} \{(\cos \frac{m}{\ell} x + \cosh \frac{m}{\ell} x) - 0.9825 (\sin \frac{m}{\ell} x + \sinh \frac{m}{\ell} x)\} \quad (2)$$

where Z is the amplitude at the position x and $Z(\ell)$ is the amplitude at $x = \ell$. The relation for fundamental frequency is shown in Fig. A2-a. The maximum in amplitude occurs at both ends. The support wires are usually connected to the outer sides of the nodal points as such positions lead to bigger resonant frequency responses. The exact distance between the support positions and the nodal point is determined by trial and error.

(b) The effect of stiffness and mass of support wires.

The natural frequency of each wire is determined by its length, mass and tension. The support wires can be troublesome because their fundamental or higher harmonics sometimes cause dummy peaks and add to the difficulty of locating the resonant frequency of the specimen. The vibrational mode of specimen may be checked by watching the motion of a light rider which is made of thin wire and is placed in an arbitrary position on the specimen. If the specimen is in resonance the rider will move to the nodal point and then remain stationary there. The length of the support wires can be so adjusted that their resonant frequencies are far away from the frequency range of resonance of specimen. The resonant frequency of wires is almost

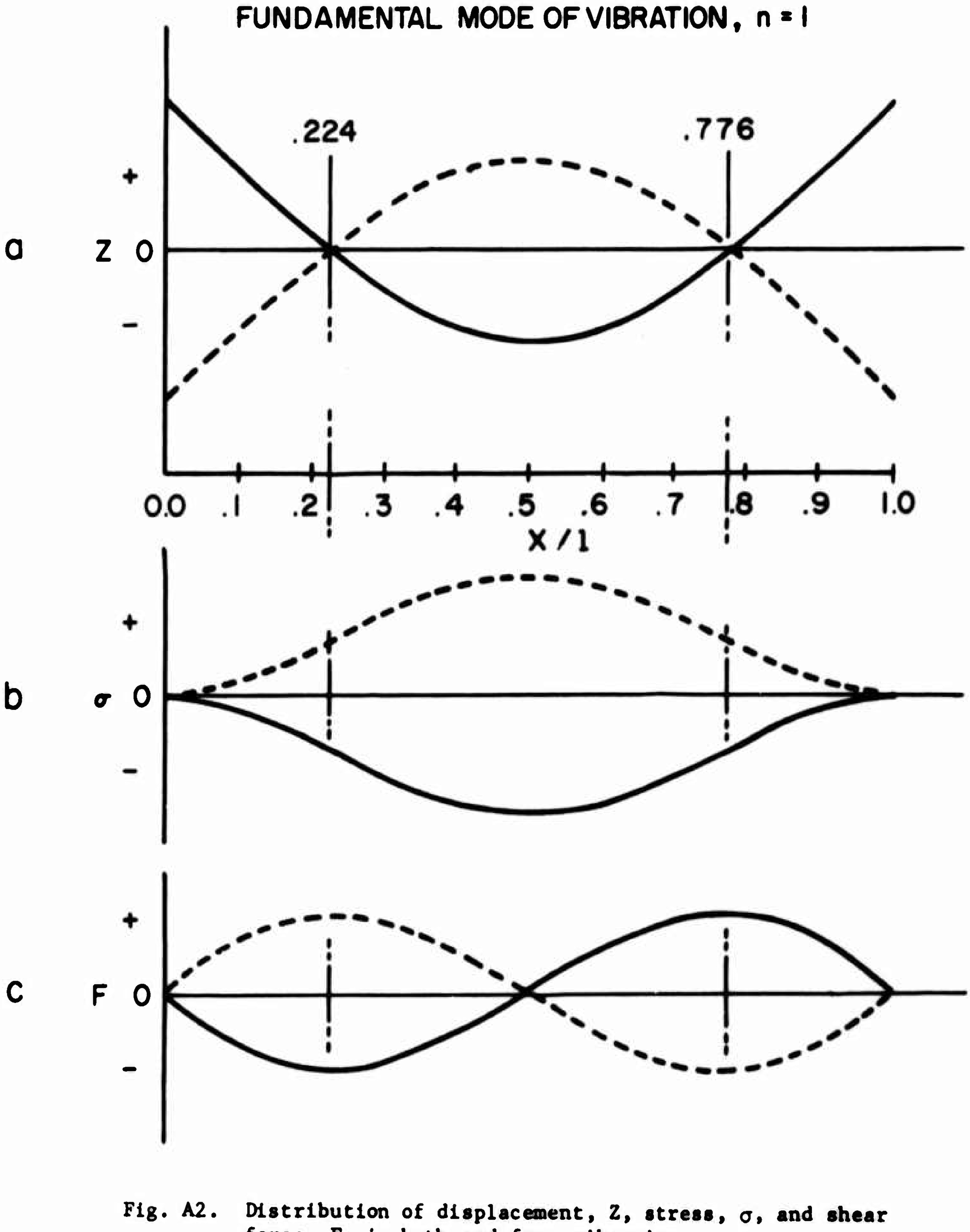

Fig. A2. Distribution of displacement, Z, stress, σ, and shear force, F, in both-end-free vibration.

impossible to calculate because of the difficulty of evaluation of the tension stress, especially for wires which are twisted or bent. Other additional vibrations which are caused by nonuniform contact between the supporting knife edge and nodal point of specimen sometimes makes the measurement much more complicated, especially at elevated temperatures. In such cases both knife edges may be removed under which condition the specimen is supported solely by the wires. The position of each wire is usually selected somewhere between the nodal point and the end of the specimen. In both-end-free vibration, the specimen should be at a standstill at the nodal points. The mechanical impedance of both wires should be negligibly small. Unfortunately, these conditions are almost impossible to obtain by calculation alone because to find out and to adjust into practice the geometrical and elastic factors which consist of stiffness and mass of wire, vibrational system of driver and detector may not be evaluated accurately. Fortunately, the optimum condition can be obtained by trial and error without much difficulty by adjusting the size and shape of the wires. Under ideal conditions, measurements of Young's modulus at elevated temperature for a given material yield identical resonant frequencies with or without the presence of supporting knife edges.

(c) Stress in specimen.

The maximum fiber stress σ for fundamental vibration is as follows:

$$\sigma = \frac{E \cdot m^2 \cdot d \cdot Z(\ell)}{4\ell^2} \left\{ \left(\cos \frac{m}{\ell} x - \cosh \frac{m}{\ell} x\right) - 0.9825 \left(\sin \frac{m}{\ell} x - \sinh \frac{m}{\ell} x\right) \right\} \quad (3)$$

The stress distribution along the length of the specimen is illustrated in Fig. A2-b, the maximum stress is present at the center of the specimen. The shear force F under the same condition is given by

$$F = - \frac{E \cdot I \cdot Z(\ell) m^3}{2\ell^3} \left\{ \left(\sin \frac{m}{\ell} x + \sinh \frac{m}{\ell} x\right) + 0.9825 \left(\cos \frac{m}{\ell} x - \cosh \frac{m}{\ell} x\right) \right\} \quad (4)$$

and is illustrated in Fig. A2-c. The maximum shear force is obtained at the nodal points.

As an example, the maximum fiber stress in silver and lead samples (4" in length and 0.2" in diameter), can be evaluated as follows corresponding to an amplitude of 0.001": 1.3×10^3 psi for silver and 0.31×10^3 psi for lead. The shear force for the same amplitude is 0.76 lb. for silver and

0.18 lb. for lead. The maximum amplitude of the specimen measured by the reading of the VTVM was calibrated with direct measurement by means of a microscope.

The stress strain relation may be more or less varied depending on the applied stress even though it is held within the so-called "elastic range". This is somewhat of a problem in such materials as lead especially at elevated temperatures. This phenomenon can be detected through the variation of resonant frequency with the amplitude at resonance. Examples of such relationships between the scale reading of the VTVM which is proportional to the amplitude, and the resonant frequencies in silver-lead alloys at room temperature are shown in Fig. 4 of the text. The value of 1.0 on the VTVM corresponds to the order of 10^2 - 10^3 psi in stress. In measuring Young's modulus, vibration of specimen should undergo as small an applied stress as possible. In this paper the resonant frequency by which Young's modulus is calculated is obtained by extrapolation of the resonant frequencies to zero amplitude; therefore, Young's modulus corresponds to the tangent at the origin of the stress-strain curve.