

Resistivity of Liquid Lead-Tin Alloys*

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The electrical resistivity of liquid lead-tin alloys has been measured as a function of temperature and composition up to 530°C by a dc potentiometric method. No anomalies were observed in the isotherms of resistivity or in the isotherms of the temperature coefficient of resistivity as a function of composition. This is in contrast to data obtained by a magnetic-induction eddy-current technique. The reported anomalies are thought to be a characteristic of the measuring technique, and may result in part from viscosity changes in the vicinity of the eutectic composition. The calculated resistivities of pure tin and lead are within about 20% of the experimental values. The experimental resistivity-composition isotherms deviate below the weighted mean values of the resistivities of the two components. The deviation is a maximum at the 50% alloy composition and varies from 2.5% at 300°C to 4% at 500°C. The shape of the isotherm is discussed in terms of the pseudopotential theory developed by Faber and Ziman. Evaluation of the substitutional-alloy formula, using the Heine and Abarenkov pseudopotential formulation and a structure factor independent of concentration, predicts that the isotherm at about 300°C should deviate by a maximum of about 2% below the weighted mean value. This is in excellent agreement with the experimentally observed resistivity deviation.

INTRODUCTION

RECENT developments¹ in the theories of electron transport have shown that the resistivity of an alloy can be calculated in Born approximation, provided the screened pseudopotential and the three structure factors associated with the alloy are known. In practice, no complete calculations have been made, because, with the exception of the alloy Cu_6Sn_5 ,² there are no systems for which all three structure factors have been measured. The pseudopotential is a volume-dependent function and, since dilatation usually occurs on alloying, a knowledge of the effect of the dilatation on the pseudopotential of each component separately would be necessary. This requirement limits the application of the general theory to very dilute alloys in which the dilatation is associated with the solute atoms only.

However, for certain systems, the general theory can be greatly simplified. The necessary conditions are that the atoms of an alloy are randomly arranged and that the three alloy structure factors are the same. It is most likely that an alloy of components having the same atomic volume, the same valency, and the same structure factors would obey these conditions. The pseudopotential of an atom in the alloy may then be taken as being the same as that in the pure metal.

The lead-tin system is one in which the atomic volume varies little with composition. The structure factors of lead and tin are also very similar,² so the system might be expected to be amenable to a simple theoretical treatment.

Although a considerable quantity of experimental resistivity data on the lead-tin system is available, much of it must be suspect, as the results of different investigators do not agree to within the claimed accuracies. Early measurements³ using the capillary technique suggested that the resistivity-composition isotherm of the liquid lead-tin system showed several departures from "normal" behavior. The compositions at which these departures occurred were related to the eutectic composition and to the limit of solid solubility. Later work by Roll and Fees,⁴ in which the electrode-less magnetic-induction technique was used, also showed unexpected variations in the resistivity, some of which were different from those previously found. The results of Roll and Fees on the lead-tin system were part of a comprehensive and detailed study of many binary alloys⁴⁻⁶ in which the resistivity-composition isotherms consistently exhibited anomalies which were related to ratios of electrons to atoms as well as to characteristics of the equilibrium diagrams. The recent work of Takeuchi and Endo,⁷ using the same technique, does not show variations of the type previously observed, and fails to agree with the data of Roll and Fees on the general form of the resistivity-composition isotherm.

It is important to establish whether or not the irregularities represent real resistivity changes. If the anomalies are substantiated, the pseudopotential theory, which at its present level of understanding predicts a smooth variation of resistivity with composition, will require considerable modification.

³ T. C. Toye and E. R. Jones, *Proc. Phys. Soc. (London)* **71**, 88 (1958).

⁴ A. Roll and G. Fees, *Z. Metallk.* **51**, 540 (1960).

⁵ A. Roll and H. Motz, *Z. Metallk.* **48**, 495 (1957).

⁶ A. Roll and P. Basu, *Z. Metallk.* **54**, 511 (1963).

⁷ S. Takeuchi and H. Endo, *Trans. Japan Inst. Metals* **3**, 35 (1962).

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¹ T. E. Faber and J. M. Ziman, *Phil. Mag.* **11**, 153 (1965).

² J. E. Enderby (private communication).

EXPERIMENTAL TECHNIQUE

A four-probe potentiometric technique was used to measure the liquid-metal resistances. The resistance cell was designed to enable resistance changes to be precisely determined as a function of temperature and composition. A schematic diagram of the cell is shown in Fig. 1. A current of about 10 mA was passed through the liquid in the capillary tube. The capillary was 12 cm long and 0.04 cm bore. This allowed a potential difference of tens of millivolts to be developed across the capillary, while keeping the current density well below the generally accepted minimum for the observation of mass-transport effects. The potential was measured to $\pm 0.5 \mu\text{V}$.

The cell was made from a borosilicate glass (Pyrex), so the upper temperature limit was held to 530°C. The current and potential probes were of molybdenum. A serious cause of error in resistance measurements by this technique arises from the formation of bubbles in the capillary from adsorbed gases. Access to the surfaces of the liquid on either side of the capillary allows a gas-pressure differential to force liquid through the capillary. This serves the dual purpose of removing gas bubbles and of examining a different sample of the liquid to check for inhomogeneities in composition.

The capillary tube was attached to the cell by a dry, ground-glass joint. The capillary length could then be defined more accurately than is possible in cells constructed using the more usual fusion process. The accuracy of the absolute values of resistivity was then mainly dependent on the constancy and accuracy of measurement of the capillary bore. The mean radius was determined from measurements of the length of a known weight of mercury in the capillary. The area of cross-section was also calculated from resistance measurements on pure mercury. The resistivity of pure mercury at 20°C was taken as 95.6 $\mu\Omega \text{ cm}$, this being the value accepted by Roll and Motz⁸ as the most common literature value. These methods of determining the "cell constant" of a given capillary agreed to within 0.5%, but to avoid any possible discrepancy between the results obtained using different capillaries, all measurements were referred to the resistivity value of mercury at 20°C.

Several resistivity-temperature curves were obtained in the initial stages of the investigation, which suggested that the resistivity-composition isotherm was not a smooth curve. Analysis of these data showed that the alloy composition in the capillary could be as much as 20 at. % different from the bulk composition, even after the system had been stirred repeatedly by bubbling gas. Thereafter, extreme care was taken to ensure that the alloy composition was constant throughout. The sliding seal on the cell, to which the capillary system was attached, facilitated mixing by mechanical means. It also enabled the capillary system to be with-

⁸ A. Roll and H. Motz, *Z. Metallk.* 48, 272 (1957).

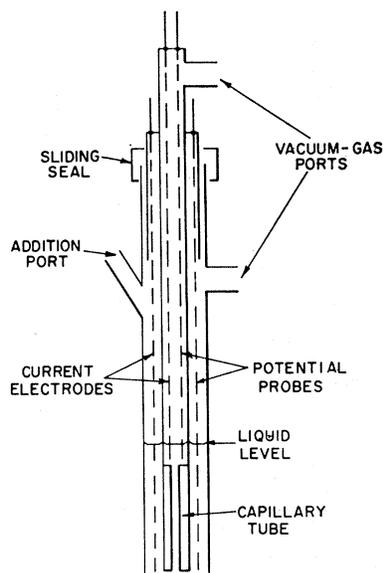


FIG. 1. A schematic diagram of the liquid-metal resistivity cell.

drawn from the liquid prior to solidification at the end of each run. Once an alloy had been mixed, no subsequent segregation arising from the difference in densities of the pure metals, or from mass transport effects, was observed.

A constant-temperature zone was maintained along the capillary, small thermoelectric effects being eliminated by reversal of the cell current. Temperatures were measured by tantalum-sheathed (Pt-13% Rh)-Pt thermocouples immersed in the liquid metal. Temperature variations greater than 0.1°C were not observed during a resistivity measurement. The variation along the cell did not exceed 0.5°C. After initially degassing the system under vacuum, measurements were performed at atmospheric pressure under a cover gas of purified helium.

Composition changes were made by adding a weighed amount of lead or tin to a liquid specimen whose weight and composition were known. After the alloy composition had been changed by 20% in small increments, a chemical analysis of the alloy was performed, and a new alloy of the same nominal composition prepared. Agreement between the chemical analyses and the resistivities of the old and new alloys of the same nominal composition was considered to be sufficient confirmation of the composition of the intermediate alloys, which were not analyzed. The purities of the lead and tin were quoted by the manufacturer, the Leytess Metal and Chemical Corporation, as better than 99.999%.

RESULTS

The resistivity measurements on lead and tin were made at approximately 10°C intervals to within a few degrees of the melting points. The resistivities at the melting points were obtained by extrapolation over not more than 5°C. The results are presented in Table I,

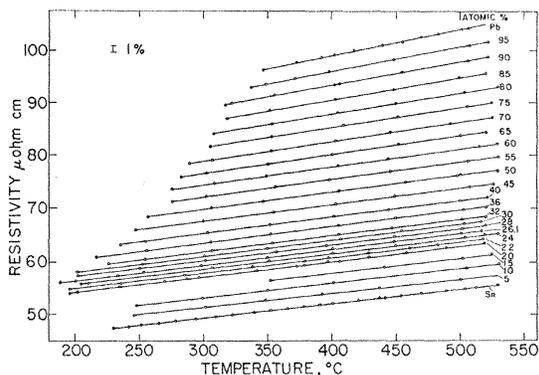


FIG. 2. Temperature dependence of the electrical resistivity of some liquid Pb-Sn alloys.

where they are compared with the data obtained by Roll and Motz,⁸ with the results of Takeuchi and Endo,⁹ and with some early work tabulated in the Liquid Metals Handbook.¹⁰

The resistivity measurements on the lead-tin alloys were made at approximately 50°C intervals from near the liquidus temperature to 530°C. The results are presented in Fig. 2. Data were obtained at composition intervals of 1 at. % in the region of the eutectic (Sn-26.1 at. % Pb) and of 2.5 at. % across the remainder of the alloy system, but for clarity alternate compositions have been omitted from the diagram.¹¹ The resistivity of lead is a linear function of temperature in the range studied. The resistivity-temperature relations of tin and lead-tin alloys are not exactly linear. The temperature coefficients of resistivity decrease by amounts up to 5% between the liquidus temperatures and 500°C, the effect being more marked as the tin concentration is increased. The variation of the temperature coefficient as a function of composition at 400°C is presented in Fig. 3. It is found to be a smooth curve which deviates negatively with respect to the weighted mean values for the pure components.

TABLE I. Resistivity of tin and lead in $\mu\Omega$ cm at various temperatures.

	Melting Point	300°C	400°C	500°C
Sn: This work	47.5	49.4	52.2	54.8
Roll and Motz (Ref. 8)	48.0	49.7	52.2	54.7
Takeuchi and Endo (Ref. 9)	46.3	47.9	50.2	52.5
Reference 10	47.6	48.7	51.4	54.1
Pb: This work	95.4	...	98.9	103.8
Roll and Motz	95.0	...	98.2	102.9
Takeuchi and Endo	96.0	...	99.2	103.6
Reference 10	94.6	...	98.0	102.6

⁹ S. Takeuchi and H. Endo, *Trans. Japan Inst. Metals* 3, 30 (1962).

¹⁰ *Liquid Metals Handbook* (Department of the Navy, Washington, D. C., 1952).

¹¹ Tables of the data are available from P. D. Adams, Brookhaven National Laboratory, Upton, New York.

The variation of resistivity with composition at 500°C is shown in Fig. 4 together with the results of some earlier work.⁴ The resistivity isotherm varies smoothly in the same manner as the temperature coefficient isotherm between the values for the pure components.

DISCUSSION

The precise shape of a resistivity-composition isotherm is of importance. The experimental results of different investigations of the lead-tin system do not agree on this point, and a detailed discussion of the results is necessary to establish which set of data is to be preferred.

Comparison of Resistivity Data

The present values for the temperature coefficients and absolute resistivities of pure lead and tin agree with the work of Roll and Motz⁸ to within the quoted limits of experimental error. The agreement with the older data¹⁰ and with the more recently published values of Takeuchi and Endo⁹ is not as good. The resistivities of lead and tin determined by Toye and Jones³ are, respectively, 15 and 30% larger than the literature values, and, as a result, the very large anomalies in the alloy resistivities observed by these workers are suspect. These data will not be considered further.

In the resistivity-composition isotherms shown in Fig. 4, the general trend of a negative deviation with respect to the weighted mean of the values for the pure metals is apparent in both curves. This is in contrast to the work of Takeuchi and Endo,⁷ who also used the magnetic-induction technique, and showed a small positive deviation. Roll and Fees⁴ observed the resistivity of pure lead to be about 3% higher than the value now found. It is also about 3.5% higher than the value found in the earlier work of Roll and Motz.⁸ This would suggest that the experimental error of the magnetic-induction technique is larger than the quoted $\pm 1\%$. Adjustment of the values obtained by Roll and Fees, on the assumption that the 3.5% represents either a

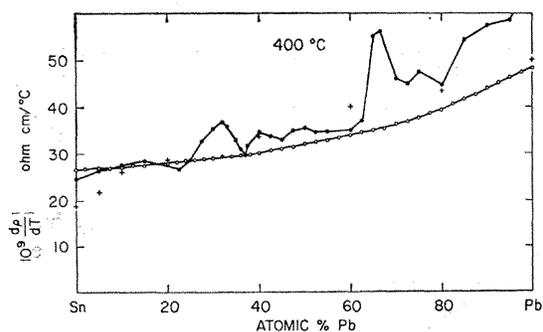


FIG. 3. Temperature coefficient of resistivity of some liquid Pb-Sn alloys as a function of composition at 400°C. ○ this work, ● Roll and Fees (Ref. 4), + Takeuchi and Endo (Ref. 7).

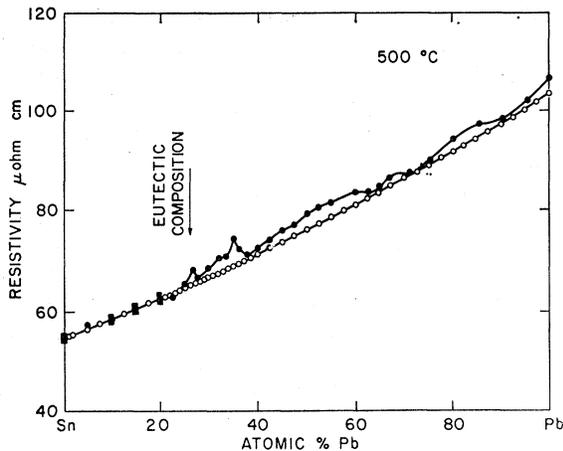


FIG. 4. Composition dependence of the electrical resistivity of some liquid Pb-Sn alloys at 500°C. ○ this work, ● Roll and Fees (Ref. 4), ■ common points.

systematic error, or an error in the pure-lead resistivity alone, does not result in agreement between these data and those of Takeuchi and Endo.

The discrepancies between the sets of resistivity data produced by Roll and Fees, Takeuchi and Endo, and the present work are shown more clearly in Fig. 5, in which the differences between the measured values and the weighted means of the values for the pure metals are presented. The present work shows a smooth curve for the resistivities which deviates by a maximum of 4% at the equi-atomic composition. None of the irregularities in the resistivity, composition isotherm of Roll and Fees are confirmed.

The isotherms of $d\rho/dT$ as a function of composition, as measured by Roll and Fees and by Takeuchi and Endo, are shown, with the present work, in Fig. 3. The irregularities found by Roll and Fees are not confirmed by the present work. The less detailed investigation of Takeuchi and Endo indicates a comparatively smooth variation of $d\rho/dT$ with composition. However, the coefficients for pure lead and tin as shown in this work differ by about 20% from the values quoted by the same workers in a previous paper,⁹ and this implies considerable uncertainty in their values determined for the alloys of lead with tin.

Discontinuous changes in temperature coefficients of resistivity or anomalies in resistivity-composition isotherms are often considered to be of significance in relation to changes in liquid structure. The absence of either of these effects in the lead-tin system suggests that the atoms are randomly arranged, with no intrinsic "structure" that changes with composition and no memory of the solid state. The reasons for the anomalies observed by Roll and Fees⁴ must be sought elsewhere.

The consistency with which anomalies appear in this and other^{5,6} alloys suggests that the experimental observations may be real, but the present work indicates

that these observations should not be interpreted simply as a resistivity effect. In the magnetic induction method, the alloy densities are required for an interpretation of the experimental observations, and these are assumed to obey the rules of simple mixing. Nonregular behavior of the density would thus be interpreted in terms of anomalous resistivities. However, resistivity is considered to be sensitive to density changes,¹² so that density change anomalies seem to be unlikely on the basis of the smoothness of the present measurements. Density anomalies in this system have been reported by Toye and Jones,³ although Fisher and Phillips¹³ found none.

Changes in viscosity could influence the interpretation of the results of the magnetic induction method without affecting the dc-resistivity data. A decrease in viscosity would result in an apparent increase in resistivity. While the effect of the change from streamline to turbulent flow is considered⁸ in the method, possible changes of viscosity with temperature or composition are apparently disregarded. A decrease in viscosity of about 7% from that of the weighted mean of the components has been observed¹³ for alloy compositions near the eutectic. Insufficient data are available to allow a quantitative determination of the effect of this viscosity change on the induction method of resistivity measurement, but it seems unlikely to account for more than 2% of the difference between the two sets of data, which differ by nearly 6% in the eutectic region. Further analysis of the magnetic induction technique does not yield an alternative explanation of the apparent resistivity anomalies.

Comparison with Theory

The present results can most readily be discussed in terms of the recent theoretical work of Faber and Ziman.¹ The substitutional model developed in this work assumes that the atomic volume is independent of concentration, that the different atom species are randomly arranged, and that the three partial structure factors can be replaced by a single structure factor $a(K)$.

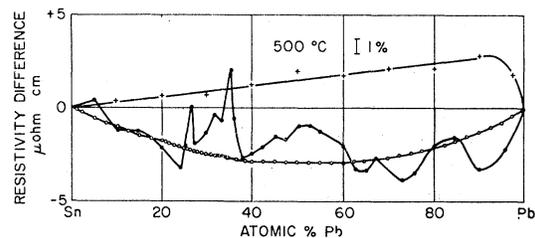


FIG. 5. Resistivity difference from the weighted mean values of the pure components of some Pb-Sn alloys as a function of composition. These curves represent the experimental values of ρ'' . ○ this work, ● Roll and Fees (Ref. 4), + Takeuchi and Endo (450°C) (Ref. 7).

¹² P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, London, 1958), Chap. 9.

¹³ H. J. Fisher and A. Phillips, *Trans. AIME* **200**, 1060 (1954).

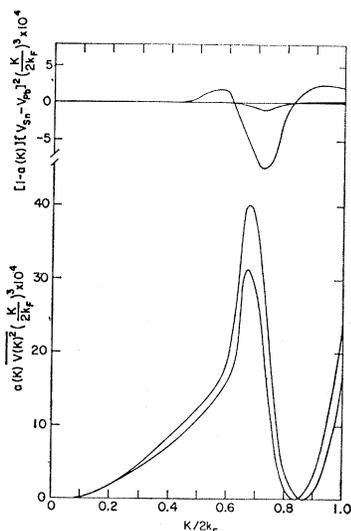


FIG. 6. A sketch of the integrands in the equations for ρ' and ρ'' . Each pair of curves represents the values taken by the integrands for a variation of 0.01 Ry in the pseudopotentials.

With these simplifying assumptions, the alloy resistivity ρ is given by

$$\rho = \rho' + \rho'',$$

where

$$\rho' = \frac{12\pi}{\hbar e^2} \frac{\Omega}{v_F^2} \int_0^1 \left\{ (1-c)a(K)[V_{\text{Pb}}(K)]^2 + ca(K)[V_{\text{Sn}}(K)]^2 \right\} \left(\frac{K}{2k_F} \right)^3 d\left(\frac{K}{2k_F} \right)$$

and

$$\rho'' = \frac{12\pi}{\hbar e^2} \frac{\Omega}{v_F^2} c(1-c) \int_0^1 \left\{ 1-a(K) \right\} \times \left\{ V_{\text{Sn}}(K) - V_{\text{Pb}}(K) \right\}^2 \left(\frac{K}{2k_F} \right)^3 d\left(\frac{K}{2k_F} \right).$$

Here Ω is the atomic volume, v_F the velocity of the electrons at the Fermi surface, k_F the wave vector of these electrons, c the atomic concentration of tin, and $V_{\text{Sn}}(K)$ and $V_{\text{Pb}}(K)$ the pseudopotentials of tin and lead, respectively.

The calculated resistivity depends very sensitively on the functions $a(K)$ and $V(K)$. The experimental determinations of $a(K)$ for $K < 2k_F$ are subject to errors of between 3 and 50% for the polyvalent metals. However, the error decreases with increasing K , and the importance of K in the resistivity equation increases towards $2k_F$, so that errors of only about 5% arise from the errors in determining $a(K)$.

TABLE II. Resistivities of Pb and Sn showing the effect of a 0.01-Ry variation in the Heine-Abarenkov (HA) potential. ρ_S is the resistivity calculated by Sundström. Values are in $\mu\Omega$ cm.

	ρ_{expt}	ρ_{HA}	$\rho_{\text{HA}} \pm 0.005 \text{ Ry}$	ρ_S
Sn (250°C)	48.0	37.3	39.5–35.7	...
Pb (330°C)	95.4	74.6	81.5–67.0	~58.4

Of rather more importance are the errors involved in the calculations of $V(K)$. Wiser¹⁴ has shown that the use of different pseudopotential formulations can, in the case of sodium, result in resistivities differing by a factor of two. For the metals Li, Na, and K, the variation of a pseudopotential within the limits of error results in resistivity changes of between 40 and 100%. These errors are somewhat reduced for the polyvalent metals. We have calculated the resistivities of pure tin at 250°C and lead at 330°C, using the structure factors determined by Enderby² and the Heine-Abarenkov pseudopotentials.¹⁵ The calculated resistivities are compared with the experimental values in Table II. The calculated values of tin and lead are both 22% lower than those observed experimentally. Consideration of the quoted error of 0.01 Ry in the pseudopotentials gives rise to between 10 and 19% variation in the resistivities. For lead, the agreement with experiment is a considerable improvement over that obtained by Sundström.¹⁶ A calculated resistivity for tin has not been reported previously.

In view of the relatively large range of values that can be obtained for the absolute resistivity of a pure metal, it might be argued that the same treatment of the alloys of lead and tin, for which the resistivity changes are quite small, would be of limited value. However, a useful analysis can be performed in terms of a comparison of the *deviations* of the calculated alloy resistivities from the calculated pure-metal values with the deviations observed experimentally. We have considered only the Heine-Abarenkov pseudopotential formulation, with the rather arbitrary assumption that another formulation would result in potentials giving roughly the same relative values although the absolute values may differ significantly.

ρ' is a linear function of concentration, and represents the straight line joining the resistivity values of the pure components, since the effects on the factor Ω/v_F^2 of the small deviations of the atomic volume from a constant value is negligible. The shape of the resistivity-composition isotherm will depend on the magnitude and sign of ρ'' . The experimental results suggest that ρ'' should be small and *negative*. Inspection of the integrand of ρ'' reveals that it will indeed be small, since $V_{\text{Sn}}(K) \cong V_{\text{Pb}}(K)$ in the heavily weighted region $k_F < K < 2k_F$. The sign of ρ'' will depend on the values of K for which $a(K) < 1$.

We have determined ρ'' using the structure factor for pure lead² at 330°C. ρ'' is a parabolic function of concentration with a maximum negative deviation of about 2% of ρ' at $c=0.5$. This is in excellent agreement with the experimental values of ρ'' , which vary between a negative deviation from the weighted mean values of 2.5% at 300°C and 4% at 500°C. Substituting the

¹⁴ N. Wiser, Phys. Rev. **143**, 393 (1966).

¹⁵ A. O. E. Animalu and V. Heine, Phil. Mag. **12**, 1249 (1965).

¹⁶ L. J. Sundström, Phil. Mag. **11**, 657 (1965).

structure factor of tin² at 250°C for that of lead does not significantly alter the value of ρ'' . This indicates that the assumption of a constant structure factor for all concentrations is reasonable.

The major error involved in the calculation of ρ'' arises from the pseudopotentials. Animalu¹⁷ has shown that the effect of nonlocal dielectric screening on the pseudopotential of lead is small, and we have considered only the computational error of about 0.01 Ry. The pseudopotential values were chosen within the limits of error to have maximum effect on the factor $\{V_{\text{Sn}}(K) - V_{\text{Pb}}(K)\}^2$ which appears in the equation for ρ'' . The value of ρ'' was found to vary from about zero to -2% of ρ' . The integrands of ρ' and ρ'' are shown in Fig. 6, in which the effects of errors in the pseudopotential are illustrated. The integrands for ρ'' are shown for the case when the pseudopotentials are shifted in opposite directions within the limits of error. The curves for ρ' represent the values taken by the integrands when the pseudopotentials are shifted in the same direction. The latter case will alter the magnitude of the calculated resistivity, but will not change the shape of the resistivity-composition isotherm. The theoretical and experimental values of ρ'' at 300°C are illustrated in Fig. 7. The curve for the calculated ρ'' represents the maximum deviation that could be obtained within the pseudopotential error limits. The calculated pure-metal resistivities are lower than those observed experimentally, so that consideration of the ratios of ρ'' to ρ' results in much closer agreement between the two cases.

These calculations indicate that the errors involved in the calculation of a pseudopotential can give rise to a wide range of resistivity values, and that the effects of the errors can be substantially reduced when relative resistivities of alloys are considered. The essential point is that the existence of a concave resistivity-composition isotherm, which was first suggested by Edwards¹⁸ and later by Faber and Ziman,¹ has been demonstrated, experimentally and theoretically, for a system whose

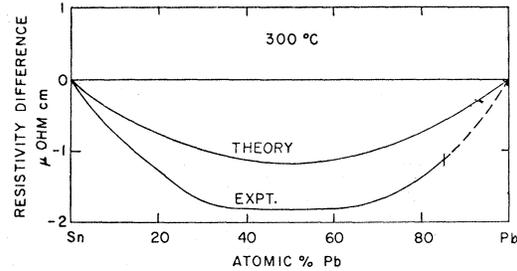


FIG. 7. Calculated values of ρ'' compared with the experiment data. Taking the ratios of ρ'' to the weighted means of the pure-metal values results in closer agreement between the two curves.

components are normally regarded as good examples of free-electron behavior. It now seems legitimate to inquire whether the "anomalous" transport properties of mercury-based alloys, for which Mott¹⁹ has developed a theoretical model, are, in fact, extreme examples of ρ'' becoming negative. To this end, an investigation is being undertaken of the application of the Faber-Ziman model to the resistivities of the mercury-based alloys,²⁰ with the help of more realistic partial structure factors derived² from the Perkus-Yevick theory of liquids.

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¹⁷ A. O. E. Animalu, *Phil. Mag.* **11**, 379 (1965).

¹⁸ S. F. Edwards, *Proc. Roy. Soc. (London)* **267**, 518 (1962).

¹⁹ N. F. Mott, *Phil. Mag.* **13**, 989 (1966).

²⁰ P. D. Adams, Ph.D. thesis, University of London, 1964 (unpublished).