IV and V on convergence of the iteration procedure and uniqueness of the solution for $S'(k)/S^2(k)$.

[26] The condition (B4) is also satisfied by the exact $g(r)$ functions of charged boson gas at high density and the hard-sphere boson system at low density.

PHYSICAL REVIEW VOLUME 187, NUMBER 1 5 NOVEMBER 1969

Calculated Electrical Resistivity of Liquid Alloys

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(Received 31 July 1969)

The electrical resistivities of several polyvalent alloy liquids were calculated from the pseudopotential form factors and Percus-Yevick hard-sphere structure factors of Ashcroft and Langreth. Good agreement with experiment was obtained by choosing hard-sphere diameter ratios other than one in four of the five systems. It is concluded that the hard-sphere structure factors with the Ashcroft pseudopotential form factors can give better agreement with experiment than have previous calculations.

INTRODUCTION

Tomlinson and Lichter[1] have reported the variation of electrical resistivity with temperature for certain compositions of molten Cd-Bi, Cd-Sn, Cd-Pb, In-Bi, and Sn-Bi. In that paper, the observed electrical resistivity was explained by using a fluctuation scattering model where the electron concentration varied with alloy composition. The deviation in electron-to-atom ratio from the normal valence was then shown to correlate with the excess free energy of mixing. In this paper, the isothermal electrical resistivity of these same alloys is calculated by using the pseudopotential method; in this case, the conduction electrons are considered to be scattered by a weak potential due to the collection of screened ions.

An expression for the electrical resistivity of a liquid binary alloy using pseudopotential form factors and structure factors (or interference functions) was written by Faber and Ziman.[2] Keating[3] had shown that the partial structure factors necessary for writing the electrical resistivity were available from experiment. However, most available structure factors have been calculated from experiments after certain approximations,[4] or are available for a limited number of alloy compositions.[5] Recently, Ashcroft and Langreth[6] and Enderby and North[7] have written partial structure factors for liquid alloys by finding the Fourier transform of the solution of the Percus-Yevick equation for a mixture of hard spheres. These structure factors were then applied to the calculation of the resistivities of several liquid alloys by Ashcroft and Langreth.[8] In this approach, the resistivity depends upon the effective core radius of the constituent potentials, the total packing fraction, the ratio of hard-sphere diameters, and the composition.

Using the notation of Ashcroft and Langreth, we have calculated the electrical resistivities of liquid alloys of the systems Cd-Bi, Cd-Pb, Cd-Sn, Sn-Bi, and In-Bi. The results are compared with the experimental values of Tomlinson and Lichter,[1] Roll and Swamy,[9] Matuyama,[10] Verhoeven and Lieu,[11] and Takeuchi and Endo.[12]

THEORY

The electrical resistivity of a liquid alloy was written by Ashcroft and Langreth[8] as

$$\rho = \frac{4\pi^3\hbar}{e^2 k_F} Z^* \int_0^1 \{X V_2^2(y) S_{22}(y) + 2[X(1-X)]^{1/2} \times V_2(y) V_1(y) S_{12}(y) + (1-X) V_1^2(y) S_{11}(y)\} y^3 dy,$$

where $V_i(y)$ is the electron-ion pseudopotential form factor for component i, Z^* is the effective valence, X is the mole fraction of component 2, $S_{ij}(y)$ is the partial structure factor, and y is the wave number divided by $2k_F$.

In these calculations, the pseudopotential form factor proposed by Ashcroft[13,14] was used. For an alloy, this is written

$$V_i(y) = \{\lambda^2 \cos(s_i y)/[y^2 + \lambda^2 f(y)]\} Z_i/Z ,$$

where $\lambda^2 = 1/\pi a_0 k_F$,

$$s_i = 2k_F R_c^{\,i} ,$$

and $f(y)$ is the Lindhard screening function. R_c is the effective ion-core radius which serves as the adjustable parameter for the pseudopotential. It may be set from appropriate experimental information (for example, the Fermi surface or ionization energy). In this instance, it was determined by the known electrical resistivities of the pure liquid metals at the melting point.

The partial structure factors were calculated using the Ashcroft and Langreth[6] representation obtained by Fourier transform of Lebowitz's[15] exact solution to the Percus-Yevick equation for a mixture of hard spheres. In their notation, the partial structure factors are written as

$$S_{11}(y) = \frac{1 - N_2C_{22}(y)}{[1-N_1C_{11}(y)][1-N_2C_{22}(y)] - N_1N_2C_{12}^2(y)} ,$$

$$S_{22}(y) = \frac{1 - N_1C_{11}(y)}{[1-N_1C_{11}(y)][1-N_2C_{22}(y)] - N_1N_2C_{12}^2(y)} ,$$

and

$$S_{12}(y) = \frac{(N_1N_2)^{1/2}C_{12}(y)}{[1-N_1C_{11}(y)][1-N_2C_{22}(y)] - N_1N_2C_{12}^2(y)} ,$$

where $C_{ij}(y)$ is the direct correlation function and N_i is the number of i atoms per unit volume.

These correlation functions are Fourier transforms of the correlation functions in real space, $C_{ij}(r)$. Details of these functions may be found in Ref. 6. The partial structure factors used here differ from those written by Faber and Ziman[2] or Halder and Wagner,[4] as was shown by Enderby and North.[7]

The procedure for calculation of electrical resistivity was first to determine the core radius R_c by solving for the resistivity of the pure metal at the melting temperature when the packing fraction η was equal to 0.456 (see Ref. 8). Table I shows the values determined. Then η was chosen for the resistivities of the pure metal at arbitrary temperatures. Finally, values for the resistivity were calculated at 10% composition intervals with various values for the ratio of hard-sphere diameters α and compared with the experimental data in order to choose the best α for each system.

TABLE I. Core radii (R_c) in Å used to calculate the pseudopotential form factors, hard-sphere radii ($\frac{1}{2}\sigma$) at melting temperature, and atomic radii (R).

Metal	R_c	$\frac{1}{2}\sigma$	R
Bi	0.803	1.56	1.54
Cd	0.744	1.36	1.49
In	0.708	1.44	1.63
Pb	0.793	1.52	1.75
Sn	0.703	1.46	1.51

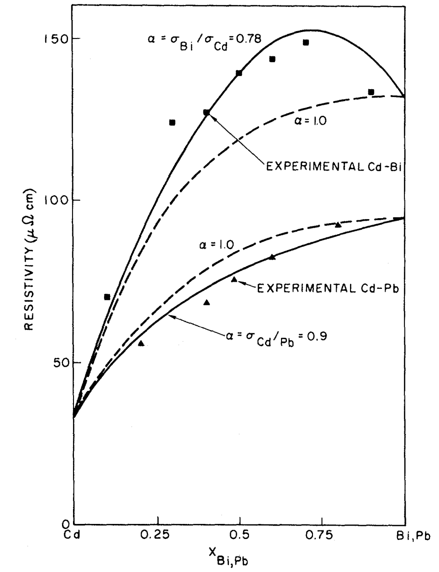

FIG. 1. Calculated and experimental electrical resistivities for liquid Cd-Bi and Cd-Pb alloys at 325 and 327 °C, respectively. Experimental points are from Tomlinson and Lichter (Ref. 1) and Roll and Swamy (Ref. 9).

RESULTS

The results for the calculated electrical resistivity for Cd-Bi at 325 °C are shown and compared with the experimentally determined values of the electrical resistivity by Tomlinson and Lichter[1] in Fig. 1. The packing fraction for the alloy was obtained by taking a linear average of the two components at each composition. Ashcroft and Langreth[8] pointed out that the η calculated by comparison of the working temperature and the liquidus temperature using $d\eta/dT$ for the components, does not differ significantly from the linear combination of the pure component packing fraction. Two calculated curves are shown: one for $\alpha = 1$, another for $\alpha = \sigma_{\mathrm{Bi}}/\sigma_{\mathrm{Cd}} = 0.78$. The latter is in general agreement with a standard deviation of 7%, but does not reproduce the asymmetry of the experimental points.

The calculated resistivity for Cd-Pb at 325 °C is shown for $\alpha = 1$ and $\alpha = \sigma_{\mathrm{Cd}}/\sigma_{\mathrm{Pb}} = 0.9$. The experimental points are those of Roll and Swamy.[9] There is good agreement when $\alpha = 0.9$ (see Fig. 1).

Similarly, the Cd-Sn system is shown with calculated points for $\alpha = 1$ and $\alpha = 0.9$ at 325 °C. Here α is the ratio of the hard-sphere diameter of cadmium to the hard-sphere diameter of tin, and the result is consistent with the trend of ionic diameters as one descends in a given column of the periodic chart. It can be seen in Fig. 2 that good agreement is obtained when $\alpha = 0.9$.

Tomlinson and Lichter[16] previously pointed out that the system Sn-Bi is virtually an ideal thermodynamic solution and that the observed electrical resistivity correlates well with a fluctuation scattering model derived from statistical mechanics. One would expect that a substitutional structure model, i.e., where atomic volumes of each constituent are equal for a particular composition, would work well with this system. However, this is not the case. In Fig. 2, the calculated electrical resistivity at 300 °C is shown for $\alpha = 1$, that is, for equal atomic diameters, and for $\alpha = 0.8$ which fits the experimental data. The experimental results are discussed in more detail in Refs. 1 and 16.

The equal-volume assumption worked well for In-Bi at 300 °C, a system which has an enthalpy of mixing estimated to be -440 cal/g atom[16] and a size difference of 15%[17] (see Fig. 3). This is the converse case to Sn-Bi since the substitutional model works well in spite of nonideal size effect and heat of mixing.

Examination of the liquid-alloy data tabulated by Hultgren *et al.*[18] and Wilson[17] showed no correlation of α with excess free energy, size difference, or electronegativity.

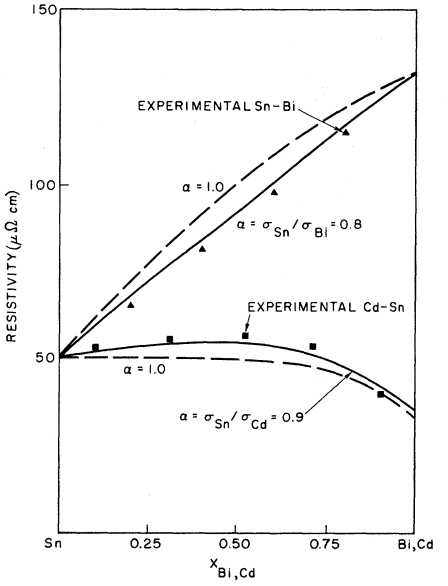

FIG. 2. Calculated and experimental electrical resistivities for liquid Cd-Sn and Sn-Bi alloys at 325 and 300 °C, respectively. Experimental points are from Matuyama (Ref. 7) and Verhoeven and Lieu (Ref. 9).

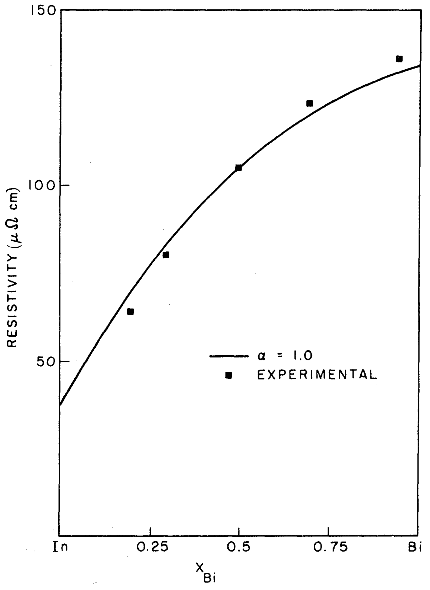

FIG. 3. Calculated and experimental electrical resistivities for liquid In-Bi alloys at 300 °C. Experimental points are from Takeuchi and Endo (Ref. 10).

DISCUSSION

We have calculated the electrical resistivity for liquid alloys of Cd-Bi, Cd-Sn, Cd-Pb, Sn-Bi, and In-Bi using the pseudopotential form factor of Ashcroft and the Percus-Yevick hard-sphere structure factors of Ashcroft and Langreth. The form factors have one adjustable parameter, the core radius, which was chosen to give the experimental electrical resistivity of the pure component at the melting temperature when the packing fraction was 0.456. The packing fraction for any arbitrary temperature was chosen by adjusting the packing fraction to fit the experimentally determined resistivity of the pure component at that temperature. Finally, the electrical resistivities for various compositions of alloys were fitted to experimental data by varying the ratio of the hard-sphere diameters of the constituents. The results for an alloy are then dependent upon the packing fraction η, the ratio α of hard-sphere diameters, and the composition X.

For pure metals, η was set at 0.456 and the core radius of the potential R_C was varied until the calculated and experimental resistivities agreed. The hard-sphere diameter was fixed, since it is the cube root of $6\eta/\pi N$, and N was determined as in Ref. 1. In Table I the hard-sphere radii are compared with the atomic radii[19] for the five elements used. One sees that the hard-sphere radii are generally lower than the atomic radii.

The values for R_C shown in Table I are consistently larger by 2% than those of Ashcroft and Langreth.[8] We suppose that this is due to a difference in the numerical integration technique.

Table II shows the packing fractions of the pure components and the calculated σ_1/σ_2 for the alloys investigated, where the order of σ_1 and σ_2 was determined by the calculated $\alpha \leq 1$, and α was found by matching the experimental alloy resistivities.

Ashcroft and Langreth did not publish a value for the core radius for cadmium. Using the procedure described above, we calculate $R_c = 0.744$ Å. When one calculates $V(y)$ using this core parameter, a potential similar to that of Animalu[20] is obtained, but crossing the y axis at $y = 0.77$ instead of 0.87. The behavior of the resistivity with changing core radius is shown in Fig. 4. It is interesting to note the strong dependence of the calculated resistivity upon the core radius.

The partial structure factors for 50 at.% Cd-Bi calculated to fit the electrical resistivity are shown in Fig. 5. It was observed that the Cd-Cd peak is dominant for $X_{\mathrm{Cd}} \geq 0.3$.

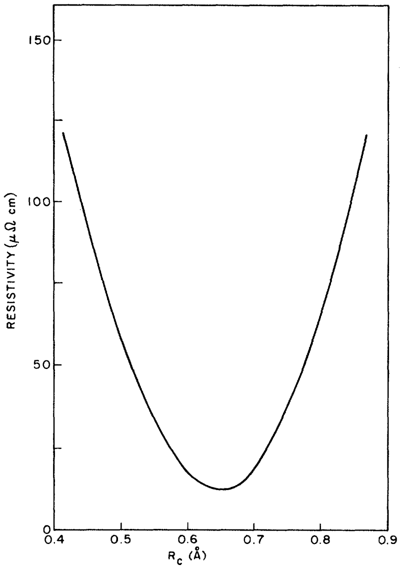

FIG. 4. Calculated electrical resistivity of cadmium plotted versus the core parameter R_c of the pseudopotential.

CONCLUSIONS

It was found that good agreement between the calculated electrical resistivities and experimental data was obtained when the hard-sphere diameter ratio was $\alpha = 1$ for In-Bi, 0.9 for Cd-Sn and Cd-Pb, 0.8 for Sn-Bi, and 0.78 for Cd-Bi; however, for the last system, the asymmetry of the experimental points was not reproduced in the calculated values.

It is apparent that for all cases except In-Bi, using the resistivity model of Ashcroft and Langreth, better calculated agreement with experimental values was obtained by allowing variation in atomic volume. One could conclude from this information that structure information in resistivity models seems to be required.

The hard-sphere model does not fit the asymmetry in experimental data for Cd-Bi. One could guess that similarly the model will not work well for systems such as Cd-Sb.[21] This points out the need for three diffraction experiments in liquid alloys.

This leads us to conclude that the Ashcroft and Langreth structure factors give improved values of calculated resistivity in liquid alloys over those obtained, assuming that the atomic volumes of both components are equal and that there is a need for more three diffraction experiments in order to obtain experimental structural information about liquid alloys.

ACKNOWLEDGMENTS

The author wishes to thank Dr. B. D. Lichter for suggesting these calculations, Dr. N. C. Halder for reading the manuscript, Dr. E. M. Dickson for pointing out an error in the Cd potential, and Dr. N. W. Ashcroft for providing prepublication copies of his papers.

TABLE II. Packing fractions and calculated hard-sphere diameter ratios.

Alloy	η_A	η_B	α
BiCd	0.44	0.456	0.78
SnCd	0.44	0.456	0.9
CdPb	0.456	0.456	0.9
BiIn	0.44	0.42	1.0
SnBi	0.44	0.44	0.8

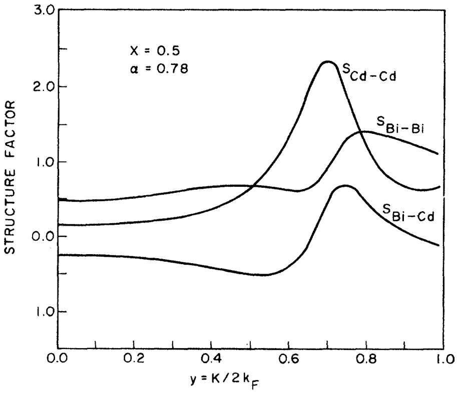

FIG. 5. Partial structure factors calculated for 50% Cd-50% Bi.

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PHYSICAL REVIEW VOLUME 187, NUMBER 1 5 NOVEMBER 1969

S-Matrix Formulation of Statistical Mechanics

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(Received 24 April 1969)

We have formulated the statistical mechanics in terms of the S matrix, which describes the scattering processes taking place in the thermodynamical system of interest. Such a formulation is necessary for studying the systems whose microscopic constituents behave according to the laws of relativistic quantum mechanics. Our result is a simple prescription for calculating the grand canonical potential of any gaseous system given the free-particle energies and S-matrix elements. When applied to a nonrelativistic gas, it gives a simple prescription for calculating all virial coefficients. Simplified relativistic gas models are considered as examples of application. A general form of the Levinson's Theorem for any number of particles follows immediately from our formalism. Its applications in statistical mechanics are briefly discussed.

I. INTRODUCTION

In this paper we present a formulation of statistical mechanics in terms of the S-matrix elements, which describes the scattering processes taking place in the thermodynamical system under consideration. The purpose of such a formulation is to be able to calculate, at least in principle, the equation of state of a relativistic system. By a relativistic system we mean a thermodynamical system whose microscopic constituents behave according to the principles of relativistic quantum mechanics. At present, the S matrix is the only quantity that can be obtained from the relativistic quantum mechanics. Therefore, to study the thermodynamical properties of relativistic systems, an S-matrix formulation of statistical mechanics is indispensable.

To our knowledge, there has been no general statistical mechanics formulated for *interacting* relativistic systems. Noninteracting systems, i.e., ideal gases, are in principle trivial to analyze. On the other hand, the statistical mechanics of interacting nonrelativistic systems has a