

## MODEL FOR THE RESISTIVITY OF LIQUID MERCURY ALLOYS\*

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Some recent theories on the electrical properties of liquid mercury-based alloys are discussed. A simple energy-dependent pseudopotential derived from the properties of pure mercury is applied to the mercury-indium system. Close agreement with experiment is obtained.

In contrast to the behavior of most liquid binary alloys, the addition of metals other than the alkalis to pure liquid mercury results in a sharp decrease in electrical resistivity.<sup>1-3</sup> Mott<sup>4</sup> proposed that a minimum in the electron density of states in the vicinity of the Fermi surface could account for the large resistivity of pure mercury. The addition of polyvalent solutes would cause the density of states at the Fermi level to approach more nearly the free-electron value by moving the Fermi surface away from the minimum and also cause the minimum to fill in. By assuming that the density of states increase is not compensated by a decrease in the mean free path, the model provides a qualitatively reasonable explanation for the observed resistivity decrease.

It has since been demonstrated<sup>3,5</sup> that provided the free-electron Fermi energy is a reasonable approximation for the Fermi energy even supposing the existence of a minimum in the density of states, the model is not consistent with all of the available experimental data, since the expected behavior with solute valence does not occur.

The simple free-electron model of Faber and Ziman<sup>6</sup> has been applied to several binary alloys by Ashcroft and Langreth<sup>7</sup> (AL). The work is based on the assumptions that the alloy structure  $a(K)$  may be approximated by the Percus-Yevick solution for the packing of hard spheres and that a simple pseudopotential formulation is a suitable approximation for the screened ion-ion interaction. The model has a somewhat greater flexibility than the original substitutional model<sup>6</sup> from the introduction of a volume dependence of the pseudopotential through the dielectric screening function. Its application to mercury-base alloys in particular requires some discussion.

It has been noted previously<sup>8,9</sup> that the calculated resistivity is highly sensitive to the detailed behavior of the pseudopotential. Using the simple Ashcroft pseudopotential<sup>10</sup> the resistivity has a parabolic dependence on  $R_{\text{core}}$ <sup>11</sup> so that there

are, in general, two values of  $R_{\text{core}}$  which will result in the same resistivity. For the alloy resistivity calculations AL chose values of  $R_{\text{core}}$  consistent with the packing fraction which, with a structure given by a hard-sphere packing fraction of 0.45, would give the experimental resistivities of the pure components at their melting points. This normalization allows a simple and direct comparison between the theoretical and experimental resistivity-composition isotherms.

Resistivity-composition isotherms were calculated for several mercury-base alloys at a number of temperatures. With  $R_{\text{core}}$  fixed by the procedure described above, the experimental resistivity of pure mercury at these temperatures was matched by selecting an appropriate value for the packing fraction. However, although the experimental resistivity of pure mercury is strongly temperature dependent, the calculated values for metals of valence 2, including mercury, are insensitive to temperature changes. This comes about because the upper limit of integration for these metals is just to the right of the first peak in  $a(K)$ . Increasing temperature causes the peak height to decrease and the intensity in the region below the first peak to increase. The weighting factor  $K^3$  in the resistivity integral is sufficient to achieve an approximate balance between these two effects and lead to a small temperature dependence of the resistivity.

The  $a(K)$  of mercury at room temperature derived by AL is illustrated in Fig. 1, where it may be compared with the experimental curve.<sup>12</sup> It can be seen that the normalization procedure of AL results in a serious discrepancy for all values of  $a(K)$  relevant to the resistivity. This is important because the partial structure factors used in the alloy calculations are strongly dependent upon the  $a(K)$ 's of the pure components.

The discrepancies at higher temperatures are greater. In Table I are listed the packing fractions chosen by AL for pure mercury at various temperatures. The compressibilities and first-peak intensities appropriate to each packing frac-

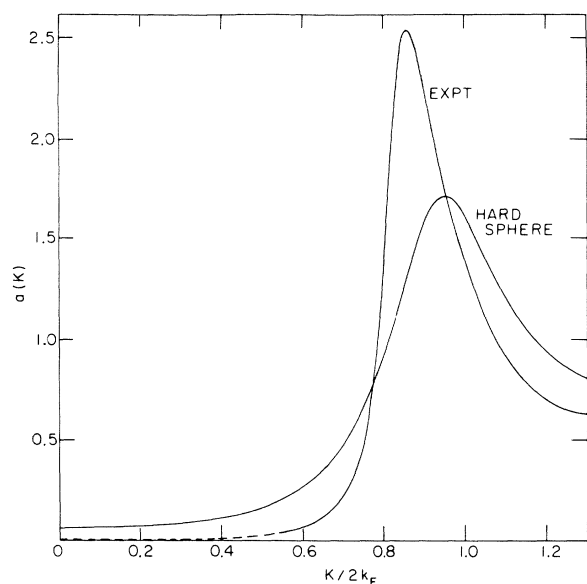


FIG. 1. Comparison with experiment of the hard-sphere structure factor for mercury chosen by Ashcroft and Langreth, Ref. 7. The experimental values are taken from N. C. Halder and C. N. J. Wagner, *J. Chem. Phys.* **45**, 482 (1966).

tion are also listed and compared where possible with experimental results. The temperature dependence of  $a(K)$  has not been extensively measured but the few published results<sup>12,13</sup> indicate that, between the melting point ( $-38^\circ\text{C}$ ) and room temperature, the decrease in the first-peak intensity is considerably less than that suggested by the AL hard-sphere packing fractions. The compressibilities of the hard-sphere liquid vary between a factor of 5 and 20 times larger than the experimental values depending on the temperature, which suggests that the first-peak intensities will also differ markedly from experiment. This means that the hard-sphere alloy structures

will bear little resemblance to the real values. The comparison of the calculated resistivities with experiment then becomes of dubious significance, and it is evident that the AL approach requires modification.

The calculated resistivity of a group-II metal is relatively insensitive to changes in packing fraction and the  $a(K)$  of mercury is, in any case, reported to be almost independent of temperature, so as a first approximation the packing fraction will be considered a constant. Agreement between the calculated and experimental resistivities at various temperatures may then be achieved by making  $R_{\text{CORE}}$  variable and, in fact, a small linear dependence of  $R_{\text{CORE}}$  upon volume is sufficient. The same volume dependence of  $R_{\text{CORE}}$  also provides reasonable agreement with the experimentally measured<sup>14</sup> variation of resistivity with pressure at constant temperature.

It has long been suggested<sup>15,16</sup> that for calculations of the thermoelectric power within the framework of the simple theory, the volume or energy dependence of the pseudopotential cannot be neglected. The observations above indicate that for mercury an energy-dependent pseudopotential (through the dependence of  $R_{\text{CORE}}$  upon volume) must be used even for the resistivity.

The densities of many nonalkali alloys of mercury have been found<sup>17,18</sup> to be larger than expected from the weighted mean values of the components. This characteristic behavior is not accompanied by large heats of solution or other evidence of molecular complexes or compounds in the liquid state. It will be assumed that this "excess" density arises from a decrease in the atomic volume of the mercury component alone. The energy dependence of the pseudopotential of pure mercury will be assumed to apply also to mercury when in the alloyed state.

Table I. The compressibility and the intensity of the first peak of the structure factor for pure mercury corresponding to the packing fraction chosen by Ashcroft and Langreth at various temperatures. The experimental compressibilities are from G. Abowitz and R. B. Gordon, *Trans. Met. Soc. AIME* **227**, 51 (1963); the first-peak intensities from R. F. Kruh, G. T. Clayton, C. Head, and G. Sandlin, *Phys. Rev.* **129**, 1479 (1963), and Halder and Wagner, Ref. 12. Hard-sphere values are denoted by H. S.

Temperature (°C)	Packing Fraction	First peak intensity		Compressibility	
		H.S.	Experiment	H.S.	Experiment
-38	0.45	2.525	~2.5	1.88	0.33
20	0.346	1.713	2.542 (25°C)	3.89	0.35
250	0.183	1.210	...	8.49	0.43
270	0.175	1.196	...	8.72	0.43
350	0.146	1.150	...	9.69	0.46

For example, in the case of the Hg-In system, the volume of the alloy Hg-20 at.%In is 0.213 ml/g atom less than the weighted mean value of the pure components. Associated with mercury alone, this corresponds to a volume decrease of 0.266 ml/g atom. The resistivity of pure mercury when compressed by this volume decreases by about 14%.<sup>14</sup> The value of  $R_{\text{core}}$  required to obtain a resistivity decreased by this amount is 0.4923, compared with 0.4813 for uncompressed mercury at the same temperature. The new value of  $R_{\text{core}}$  is then used to calculate the resistivity of the alloy Hg-20 at.%In.

This procedure, repeated at different compositions, results in the dotted curve in Fig. 2. The initial rapid decrease in the experimental resistivity with increasing indium concentration is well reproduced. As might be expected, the agreement is less good at high indium concentra-

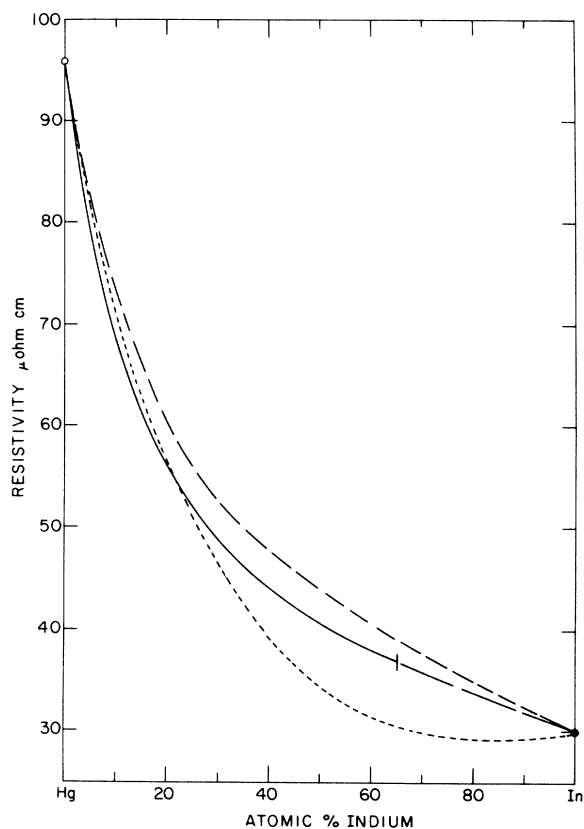


FIG. 2. The variation of resistivity with composition for the Hg-In system at room temperature. The dotted curve represents the values calculated using a hard-sphere structure factor and an energy-dependent pseudopotential. When modified by the measured Hall coefficient (Ref. 1) the dashed curve is obtained. The full line represents the experimental resistivities (see Ref. 1).

tions where the density changes assumed to be associated with the mercury component alone become quite large and the estimations of  $R_{\text{core}}$  less certain.

Some error in determining  $R_{\text{core}}$  is introduced by the use of an unmodified hard sphere  $a(K)$  for polyvalent metals, even though it provides an excellent representation of the structure of the alkali metals. In the region of wave number space below the first peak position  $a(K)$  for a polyvalent metal at its melting point is about a factor of 3 too large (the experimental value being  $\sim 0.01$ ). Although the resistivity integral is heavily weighted towards the upper limit of integration, significant discrepancies in the resistivities may still appear. The resistivity of indium, for example, calculated with the experimental  $a(K)$  is  $30.2 \mu\Omega \text{ cm}$  compared with  $37.8 \mu\Omega \text{ cm}$  for the hard sphere  $a(K)$  and the same pseudopotential. Fortunately, the composition dependence of the resistivity of an alloy, which is the main point of this Letter, arises mainly from the term  $1-a(K)$ . Since  $a(K)$  is small in the region where the discrepancies between the hard sphere and the experimental  $a(K)$  are large, the term  $1-a(K)$  and hence the composition dependence of resistivity are not greatly affected by the use of the hard-sphere approximation for the alloy structure.

The alloy resistivities have been calculated assuming that the component metals retain their normal valences. However, the experimental Hall coefficients of many mercury-based alloys including the Hg-In system<sup>1,19</sup> indicate that in the free-electron approximation the number of conduction electrons is larger than expected from the normal valences of the components. The resistivity calculated using these measured values for Hg-In is shown as the dashed curve in Fig. 2. Again, the initial rapid decrease in resistivity with increasing indium concentration is closely reproduced. In addition, the agreement with the values at higher indium concentrations is much improved, the maximum difference between the curves being  $5 \mu\Omega \text{ cm}$ .

It is now apparent that the electrical resistivities of mercury and its alloys can be satisfactorily explained within the framework of the Faber-Ziman theory, provided that the mercury pseudopotential is assumed energy dependent. Data on the temperature dependence of  $a(K)$  of mercury would be most useful in applying the model to other mercury alloys, since the assumption of 0.45 for the packing fraction is unlikely to hold at higher temperatures. The degree of agreement

between the experimental and calculated resistivities, when using the valence given by the measured Hall coefficient, suggests that the number of conduction electrons in the alloy may indeed be larger than expected from the normal valences. The volume dependence of the Hall coefficient at constant temperature of pure mercury would greatly assist the solution to this question.

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## ANOMALOUS PHONON EFFECTS ON SPECIFIC HEAT AND SPIN-LATTICE RELAXATION IN CERIUM ETHYL SULFATE\*

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The hitherto unexplained extra specific heat and fast spin-lattice relaxation in cerium ethyl sulfate are explained by an anomalous phonon spectrum calculated using thermodynamic Green's functions for incoherent spins and phonons.

For the  $\text{Ce}^{3+}$  ion in cerium ethyl sulfate (CES), the lowest crystal-field states are the three  $J = \frac{5}{2}$  Kramers doublets. The first excited doublet is at  $E_0 = 6.8^\circ\text{K}$  above the ground doublet and the second excited doublet is at  $E_1 \approx 150^\circ\text{K}$ .<sup>1,2</sup> Near the peak of the Schottky specific heat associated with the two lowest  $\text{Ce}^{3+}$  doublets, there is a hitherto unexplained contribution. After subtracting the normal lattice specific heat, the entropy calculated<sup>3,4</sup> (from what should be the residual  $\text{Ce}^{3+}$  specific heat associated with the two lowest doublets) is greater than  $R \ln 4$  for  $T > 12^\circ\text{K}$ . This cannot be accounted for by the population of the doublet at  $E_1 = 150^\circ\text{K}$ .

To explain the extra specific heat and entropy, perturbation and Green's function calculations based on strong spin-phonon interaction have been attempted by a number of authors.<sup>5,6</sup> In all these calculations the two doublets are treated as an effective spin- $\frac{1}{2}$  state whose levels are split by an energy  $E_0$ . Rather than the general spin-phonon interaction, a linearized interaction is used. The Hamiltonian then has the form

$$\mathcal{H} = -E_0 \sum_{i=1} S_{iz} + \sum_{\vec{k}, p} E_{\vec{k}p} (a_{\vec{k}p}^\dagger a_{\vec{k}p} + \frac{1}{2}) + \frac{1}{\sqrt{N}} \sum_{L=1}^N \sum_{\vec{k}, p} A_{\vec{k}p} \exp(i\vec{k} \cdot \vec{r}_i) (a_{\vec{k}p}^\dagger + a_{-\vec{k}p}) (S_{i+} + S_{i-}), \quad (1)$$

where  $S_{iz}$  and  $S_{i\pm}$  are spin operators at lattice site  $i$ ,  $N$  is the number of spins,  $N_L$  is the number of unit cells,  $a_{\vec{k}p}^\dagger$  and  $a_{-\vec{k}p}$  are phonon creation and annihilation operators,  $E_{\vec{k}p}$  is the energy of a phonon with wave vector  $\vec{k}$  and polarization  $p$ , and  $A_{\vec{k}p}$  is the spin-phonon coupling energy. Because of the phase factor  $\exp(i\vec{k} \cdot \vec{r}_i)$  in the Hamiltonian, the elementary excitations at different lattice sites are