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EXPERIMENTAL EVIDENCE FOR THE INADEQUACY OF THE BASIC FORMULA FOR THE ELECTRICAL RESISTIVITY OF A LIQUID METAL

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The purpose of this Letter is to present experimental evidence, from x-ray diffraction data on liquid Na, that the basic formula for the electrical resistivity of liquid metals is inadequate. We shall examine the assumptions of this formula with an eye to determining the source of the inadequacy.

The electrical resistivity ρ of liquid metals calculated in Born approximation is given by the formula first advanced by Ziman,¹

$$\rho = \frac{4\pi^3 \hbar z}{e^2 k_F} \int_0^1 a(x) |v(x)|^2 x^3 dx. \quad (1)$$

In Eq. (1), z is the valence, k_F is the Fermi momentum, $a(x)$ is the static structure factor, and $v(x)$ is the screened electron-ion potential. We have made the integral dimensionless by scaling $v(x)$ to $\frac{2}{3} E_F$, the Fermi energy, and introducing $x = q/2k_F$ as the variable of integration, where q is the momentum transfer. In these units, $v(0) = -1$. We have chosen to test the formula for ρ by determining the temperature coefficient α which is defined by

$$\rho(T)/\rho(T_0) = 1 + \alpha(T - T_0). \quad (2)$$

For this purpose we have made a careful measurement of $a(x)$ of liquid Na as a function of temperature and used our measurements to calculate α . We find a marked discrepancy between theory and experiment of almost a factor of 2.

Virtually the entire contribution to α arises from the temperature dependence of $a(x)$. In Fig. 1, we show the ratio $r_T(x) \equiv a_T(x)/a_{102^\circ\text{C}}(x)$, as determined by our x-ray diffraction measurements. In Eq. (1), the quantities k_F and $|v(x)|^2$ are also temperature dependent because of their density dependence, but they contribute little to α .² We have calculated the temperature coefficient α_{calc} for several poten-

tials, and in Table I we show the ratio of α_{calc} to the experimental value α_{expt} . As we can see, α_{calc} is much smaller than α_{expt} for all of these potentials. In fact, no choice of potential will bring agreement between α_{calc} and α_{expt} . A detailed analysis of the integrand shows that the high- x region makes the dominant contribution to the integral in Eq. (1).³ In that region, the ratio $r_T(x)$ is significantly smaller than the corresponding ratio of the resistivities. For example, $r_{207^\circ\text{C}}(x)$ varies from 1.28 to 1.02 in the important region of integration $0.4 < x < 1.0$. The corresponding resistivity ratio $\rho(207^\circ\text{C})/\rho(102^\circ\text{C})$ is 1.42. Focusing our attention on α thus has the advantage of providing a clear-cut test of Eq. (1), independent of the choice of potential. This is in marked contrast to the sensitive dependence of the resistivity itself on the precise form of $v(x)$.³ Therefore, our conclusion that α_{calc} is much less than α_{expt} is valid for any potential.

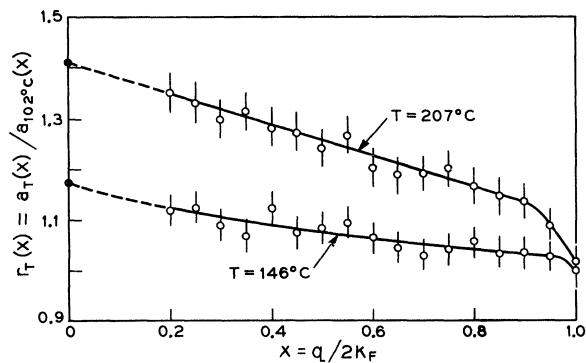


FIG. 1. The temperature dependence of $a(x)$ of liquid Na is shown by plotting the ratio $a_T(x)/a_{102^\circ\text{C}}(x)$ as a function of x . The error bars represent the 3% relative error. The measurements were carried out for $x > 0.2$. The point at $x = 0$ is known from theoretical considerations.

Table I. Ratio of the calculated to the experimental value of the temperature coefficient of electrical resistivity of liquid Na over the temperature range 102-207°C. The value of α_{expt} is 0.0040/°C.

Source for potential $v(x)$	Pseudo-potential ^a	Model potential ^b	Phase-shift analysis ^c
$\alpha_{\text{calc}}/\alpha_{\text{expt}}$	0.57	0.59	0.48

^aW. A. Harrison, Phys. Rev. **136**, A1107 (1964).

^bL. J. Sundström, Phil. Mag. **11**, 657 (1965). I wish to thank Dr. Nathan Wisner for sending me the numerical values of the model potential calculated by Dr. Sundström.

^cSee Ref. 6.

The basic equation for ρ , Eq. (1), rests on five assumptions: (1) The Boltzmann equation is valid. (2) The Born approximation may be used to calculate the collision term in the Boltzmann equation. (3) The solution to the Boltzmann equation is adequately given by the simplest trial function in a variational calculation. (4) The Fermi surface is spherical. (5) Since Eq. (1) is the high-temperature limit of the general expression for the resistivity,⁴ we assume that the liquid phase of Na corresponds to the high-temperature regime. Kohn and Luttinger have shown that assumption (1) is valid for liquid Na,^{5,6} if assumption (2) is true. As is well known, the small excursions of the ions from their equilibrium position justifies assumption (2) for the solid phase of a metal, and many theorists have made this assumption for the liquid phase also.⁷ Assumptions (3) and (5) are numerical approximations which have been explicitly verified for liquid Na by Greene and Kohn.⁶ Even for the solid, assumption (4) has been adequately demonstrated both experimentally and theoretically. In view of the wide acceptance of these assumptions, one hesitates to question them.

Our data for $a(x)$ were taken using monochromatic Cu radiation of wavelength 1.542 Å. Rather than the usual method of reflection, we used x-ray transmission through a cell 0.5 mm thick having 0.025-mm Be walls. Our method is better suited for obtaining $a(x)$ in the region relevant to Eq. (1), $x < 1$. For the wavelength used, this corresponds to scattering angles less than 25°. The necessary corrections were made for polarization, incoherent scattering, atomic form-factor normalization, absorption, and empty-cell scattering.

The last two corrections were made using a direct measurement of the absorption of each cell. For determining α , only the temperature dependence of $a(x)$ and not the absolute magnitude is required. Therefore, the sources of error in our experiment which stem from normalization of $a(x)$ are unimportant, because they affect only the absolute magnitude. We have taken pains to assure ourselves that there are no spurious contributions to the observed diffraction patterns. A complete description of the experimental arrangement will be published separately. With a given cell, $a(x)$ was reproducible to within 2% relative error. This is about the expected statistical counting error. A comparison of data taken from cells of somewhat different thicknesses still led to only 3% relative error. The 3% relative error in $a(x)$ yields a 15% error in α_{calc} . The observed discrepancy between α_{calc} and α_{expt} of a factor of 2 is thus far outside the experimental error.

There have been four previous determinations of $a(x)$ for liquid Na as a function of temperature. However, none of these is adequate for calculating α , because they do not provide a sufficiently accurate determination of $a(x)$ for $x < 1$. Since in each of these cases the experiment was designed to provide data primarily in the range $x > 1$, the inadequacies subsequently discussed do not in any way imply that the experiments were not adequate for the purpose intended. The most widely used measurement of $a(x)$ for resistivity calculations is the neutron-diffraction data of Gingrich and Heaton.⁸ However, we believe that the neutron-diffraction data suffers from two main difficulties. First and foremost, multiple scattering is not isotropic as was assumed. Second, the data were taken as a function of angle and converted to a function of x on the assumption of elastic scattering, which is not the case. This is evident from the work of Randolph⁹ who made careful measurements of the partial differential cross section for slow-neutron scattering from liquid Na. From Randolph's data, one can also determine $a(x)$, and he has, in fact, done so. However, Randolph has pointed out that in the region $x < 1$, the finite angular resolution of his detector leads to considerable error. Another determination of $a(x)$ versus temperature was that of Orton, Shaw, and Williams¹⁰ using x-ray reflection. In contrast to the neutron-diffraction data, multiple scat-

tering of x-rays is negligible and also, the scattering is very nearly elastic. However, the experiment of Orton, Shaw, and Williams failed to cover the region relevant to the integration, their lowest value for x being 0.7. The earliest determination of $a(x)$ was made by Trimble and Gingrich¹¹ using x-ray transmission. However, the experimental techniques available 25 years ago, such as the microphotometry of film, are far less accurate than modern counting techniques. Although previous determinations of $a(x)$ indicated deviations between α_{calc} and α_{expt} , a point which had been emphasized by Greene and Kohn,⁶ we believe that the nature of these earlier determinations of $a(x)$ was such that the existence of a discrepancy had not been conclusively established.

In summary, we believe that our measurements of $a(x)$ clearly demonstrate that a serious disagreement between the best accepted current theory and experiment exists. In the absence of some other convincing explanation for this discrepancy, we conclude that these results are evidence for the breakdown of the Born approximation in liquid metals.

We wish to thank Professor Volker Heine for suggesting this experiment, and we express our gratitude to Professor Walter Kohn and Professor J. M. Luttinger for several illuminating discussions. We also wish to thank Dr. Nathan Wiser and Dr. Paul Soven for many

useful conversations. Finally, we wish to acknowledge the help received from Dr. George Brady and Professor Boris W. Batterman on the experimental aspects of the problem.

¹J. Ziman, *Phil. Mag.* **6**, 1013 (1961).

²Over the temperature range we are considering, the experimental value of α is 0.0040/°C whereas the contributions to α from k_F and $|v(x)|^2$ are only 0.000 09/°C and 0.000 12/°C, respectively. The contribution of $|v(x)|^2$ to α was calculated using the method outlined in Section IV of Harrison's paper [W. A. Harrison, *Phys. Rev.* **131**, 2433 (1963)].

³N. Wiser, *Phys. Rev.*, to be published.

⁴G. Baym, *Phys. Rev.* **135**, A1691 (1964).

⁵W. Kohn and J. M. Luttinger, *Phys. Rev.* **108**, 590 (1957).

⁶M. P. Greene and W. Kohn, *Phys. Rev.* **137**, A513 (1965).

⁷See, for example, Baym, Ref. 4, and I. Mannari, *Progr. Theoret. Phys. (Kyoto)* **26**, 51 (1961). In fact, since the Ziman expression, Eq. (1), is just the Born-approximation result, all the recent resistivity calculations for liquid metals, such as L. J. Sundström [*Phil. Mag.* **11**, 657 (1965)], have implicitly assumed the validity of the Born approximation.

⁸N. S. Gingrich and L. Heaton, *J. Chem. Phys.* **34**, 873 (1961). I wish to thank Dr. Heaton for sending me the data for $a(x)$ at 325°C which were not reported in their paper.

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¹⁰B. R. Orton, B. A. Shaw, and G. I. Williams, *Acta Met.* **8**, 177 (1960).

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LAMBDA TRANSITION IN ADSORBED HELIUM AT $T > T_\lambda \dagger$

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A growing recent interest in the properties of adsorbed helium¹⁻⁸ has led us to re-examine an unsolved problem in earlier work. Our measurements indicate that a phase transition corresponding to the lambda transition in bulk He⁴ occurs in the adsorbed film at temperatures above T_λ for pressures below the bulk vapor pressure (hereafter P_0). The temperature and pressure coordinates of the transitions form a curve in the P - T plane which is an extension of the lambda line into the region of the unsaturated film (i.e., at $P < P_0$).

In 1949 the heat capacity of multilayer films of adsorbed He⁴ was measured by Frederikse.⁹

He found that the maximum in the heat capacity due to the lambda transition was depressed in temperature, and the anomaly broadened with decreasing coverage. In 1951 Morrison and Drain¹⁰ found substantially similar results for adsorbed argon near the melting point of the bulk solid. Meyer and Long¹¹ then pointed out that for such systems the surface tension must be treated as an additional intensive thermodynamic variable—a two-dimensional analog of pressure. This allows for the coexistence of three phases, two adsorbed phases and the vapor, along a line in the P - T plane at $P < P_0$. The heat capacities are measured at constant