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Isothermal Compressibility and the Structure Factor of Liquid Alkali Metals*

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Data and calculations are presented which indicate that the isothermal compressibility of alkali metals is determined mainly by the repulsive part of the ion-ion potential. The speed of sound in rubidium was measured over the temperature range 56–260° C, and the isothermal compressibility, κ_T, was calculated. An effective hard-sphere diameter, σ, was determined by using the experimental value of κ_T in the compressibility relation obtained from the hard-sphere solution of the Percus-Yevick equation. Agreement with the values of σ obtained by Ashcroft and Lekner from neutron diffraction data is good. The hard-sphere structure factor based on values of σ obtained from compressibility data was used to calculate the temperature dependence of the resistivity of liquid rubidium. Finally, using the hard-sphere model, the concentration dependence of the compressibility of Na-K alloys was calculated.

INTRODUCTION

According to pseudopotential calculations[1] the total energy of a metal can be written as the sum of a term representing pairwise interactions between electronically screened ions and other terms, such as the energy of the electron gas, which depend only on the average density of the ions. The magnitudes of the repulsive and attractive parts of the ion-ion potential are comparable with those of rare-gas liquids.

Ashcroft and Lekner[2] (hereafter referred to as AL) have suggested that the principal factor determining the arrangement of the ions in a liquid metal is the ion-ion repulsion. They approximated this interaction by a hard-sphere potential. The known solution of the Percus-Yevick equation[3] for the hard-sphere potential was fitted to the first peak of the liquid structure-factor curve $a(k)$. The fit was made as a function of the effective packing density of the fluid described by the parameter η, the fraction of the total fluid volume occupied by the spheres:

$$\eta = (\pi/6)n\sigma^3 , \tag{1}$$

where σ is the hard-sphere diameter and $n = N/V$ is the number density, N being the number of ions in volume V. AL determined the value of η for various liquid metals. The value of η used by AL for a particular metal at a given temperature is that value for which the calculated hard-sphere structure factor agrees best with the experimental $a(k)$ determined from x-ray and neutron diffraction data. Using the hard-sphere structure factor corresponding to this value of η, AL were able to account for the resistivities of liquid metals on the basis of a theoretical expression derived by Ziman.[4]

The recent molecular dynamics calculations of Verlet[5] provide further evidence supporting the use of a hard-sphere model to reproduce the structure factors of simple liquids. These calculations, made for a system of particles interacting through a Lennard-Jones potential, show that the form of the various correlation functions at high density (typical of liquids near the melting point) is due mainly to the geometrical effects produced by the existence of a strong repulsion in the potential. These effects are adequately displayed by the solution of the Percus-Yevick equation for a hard-sphere potential.

The Percus-Yevick equation also yields, for the hard-sphere fluid, the following relation between η and the isothermal compressibility κ_T;

$$nkT\kappa_T = (1-\eta)^4/(1+2\eta)^2 . \tag{2}$$

For sodium near the melting point the hard-sphere κ_T calculated from Eq. (2) is in good agreement with the experimental value. For the polyvalent metals, however, the experimental compressibilities differ considerably from the corresponding hard-sphere values. AL conclude that the compressibility of alkali metals is determined mainly by the ion-ion repulsion, and hence the hard-sphere relation between η and κ_T is valid for these metals. They use this relation to determine the temperature variation of η in sodium from the experimentally known temperature variation of κ_T. The corresponding hard-sphere structure factors were then used in the theoretical expression of Ziman to successfully reproduce the temperature dependence of the resistivity of liquid sodium.

COMPRESSIBILITY AND THE EFFECTIVE HARD-SPHERE DIAMETER

The present measurements of the compressibility of liquid rubidium were undertaken to further test the applicability of Eq. (2) to the alkali metals, and, in particular, to see whether Eq. (2) can be used to determine the temperature variation of η from compressibility data. Rubidium was chosen for this work since neutron diffraction data[6] for this metal is available over the temperature range 40–360°C. AL determined the temperature dependence of η in liquid rubidium directly from diffraction data, and calculated successfully its electrical resistivity as a function of temperature.

In the present investigation, in order to obtain the isothermal compressibility, the speed of sound, c, was measured in molten rubidium over the temperature range 56–260°C. This measurement was made using a 45.00-MHz ultrasonic signal and a phase comparison technique similar to that described by Bockris and Richards.[7] The rubidium, 99.9% pure, was obtained from MSA Research Corporation in glass ampoules sealed under an argon atmosphere. The metal was transferred directly from the ampoule to the ultrasonic interferometer and then kept under an argon atmosphere throughout the experiment. The measured sound velocity was observed to decrease linearly with temperature, the data being best fitted by the straight line

$$c = 1.2755\times 10^5 - 39.87T\ , \tag{3}$$

where T is the temperature in °C and c is in cm/sec. The maximum error in c is estimated to be less than $\pm 0.2\%$.

The value of κ_T is calculated from the relation[7]

$$\kappa_T = (c^2\beta^2 TM/C_p + 1)/c^2 d\ , \tag{4}$$

where d is the density, β the thermal expansivity, C_p the molar heat capacity at constant pressure, and M the atomic weight. The number density, n [see Eq. (1)], and the thermal expansivity, β, are calculated from density data. The density of liquid rubidium has been measured by a number of investigators.[8–12] Calculations were made using the density data of each investigator, but only extreme values of the results are given in the tables. The C_p data were taken from Ref. 9.

The values of n and κ_T are summarized in Table I. These are used in Eqs. (1) and (2) to calculate η and the hard-sphere diameter σ. These calculations are presented in Table II and compared with the results obtained by AL from neutron diffraction data. As can be seen from Table II, the values of η calculated from Eq. (2) are in good agreement with the values obtained by AL. The temperature derivatives, however, are somewhat different, the $d\eta/dT$ calculated from the different sets of compressibility data being from 12 to 24% higher than the $d\eta/dT$ calculated from the data of AL. It is difficult to determine whether this difference in the values of $d\eta/dT$ is significant or within the limits of experimental error. The spread in the values of κ_T points to the need for more accurate density data. Furthermore, it is not easy to assess the accuracy of the neutron diffraction data. Finally, there has been little discussion of the precision with which η may be obtained by fitting the hard-sphere solution for $a(k)$ to the first peak of the experimental diffraction data.

TABLE I. Temperature dependence of the compressibility of liquid rubidium. The ranges of compressibility values correspond to extreme values obtained from density data reported in Refs. 8–12.

T (°C)	Number density n (10^{22} ions/cm^3)	Isothermal compressibility κ_T (10^{-12} cm^2/dyn)
40	1.031–1.062	46.2–49.4
160	0.993–1.024	53.8–57.0
240	0.967–0.998	59.6–63.3
360	0.929–0.959	67.0–74.4

TABLE II. Temperature dependence of the hard-sphere packing parameter and the hard-sphere diameter of liquid rubidium.

T (°C)	Hard-sphere packing parameter η		Hard-sphere diameter σ (10^{-8} cm)	
	From κ_T data	AL	From κ_T data	AL
40	0.464–0.472	0.459	4.38–4.43	4.33
160	0.418–0.424	0.412	4.28–4.32	4.24
240	0.391–0.396	0.395	4.22–4.26	4.22
360	0.353–0.363	0.365	4.13–4.18	4.17

TEMPERATURE DEPENDENCE OF RESISTIVITY

It is of interest to calculate the temperature dependence of the resistivity of liquid rubidium using the hard-sphere $a(k)$ based on values of η obtained from compressibility data. According to the Ziman theory of electronic transport properties for liquid metals, the resistivity ρ may be calculated from

$$\rho = (4\pi^3\hbar/e^2 k_F)Z\int_0^1 x^3 a(x)V^2(x)dx\ , \tag{5}$$

where $V(x)$ is the electron-ion pseudopotential in units of $\frac{2}{3}E_F$ and x is the wave-number variable expressed in units of $2k_F$. Z is the valence, and $a(x)$ is the structure factor of the liquid metal. The pseudopotential used in Eq. (5) was the particularly simple potential recently described by Ashcroft,[13] and used successfully in calculations of resistivity of binary alloys. In r space this potential has the form $V(r) = -Ze^2/r$ for $r > R_{\text{core}}$, and $V(r) \approx 0$ for $r < R_{\text{core}}$, where R_{core} is an effective ion-core radius. This potential was screened locally in the way suggested by Heine and Abarenkov.[14]

The various effects which lead to a volume dependence of the pseudopotential are described by Ziman.[4] In the present investigation the simplifying assumption is made that R_{core} remains constant as the density of the metal decreases with temperature. Thus it is assumed that the bare potential of the ion is independent of volume, and the change in the pseudopotential is due to a shift in the value of k_F and to the volume dependence of the dielectric function. For rubidium the value $R_{\text{core}} = 1.12$ Å was taken from the work of Ashcroft and Langreth.[15]

Resistivity calculations were made using two sets of values of κ_T. These κ_T values were obtained from density data presented in Refs. 10 and 11 along with the speed of sound data of Eq. (3). These sets of κ_T values were chosen since they lead to the lowest and highest values respectively of the derivative $d\eta/dT$. Also, for comparison, ρ was calculated using the hard-sphere structure factor determined by AL. The results are plotted in Fig. 1. The agreement between experimental and calculated values is quite good. However, the values of ρ based on density data of Ref. 11 deviate noticeably from a linear temperature dependence. The experimental temperature dependence of ρ plotted in Fig. 1 is taken from AL. It is in good agreement with the recent data of Ref. 9 and with the data of several other investigators, referred to in Ref. 9. (The experimental values of Endo,[16] however, lead to a temperature derivative, $d\rho/dT$, which is some 20% lower than that in Fig. 1.)

It has been suggested[4] that, rather than compare absolute values, it is more meaningful to compare the measured and calculated values of the dimensionless coefficient $(T_m/\rho_m)\,(d\rho/dT)_p$ where T_m and ρ_m are the melting point temperature and resistivity, respectively. In this manner, possibly, one can reduce some of the errors that might arise in using the wrong pseudopotential in calculating the absolute value of ρ. Values of this coefficient are given in Table III. Again the agreement between experimental and calculated values is good.

COMPRESSIBILITY OF BINARY ALLOYS

The above discussion has been restricted to pure metals. Recently Ashcroft and Langreth[15] have extended the hard-sphere approach to calculation of the structure factors of binary systems, for which the Percus-Yevick equation has been solved.[17] They were able to show that, in addition to accounting for the resistivity of the pure metals, the hard-sphere approach is able to account for the deviation of the resistivity in the binary alloys from the value that would be expected on the basis of a linear extrapolation between the pure metal values. For one of the alkali-metal binary alloys, namely Na-K, compressibility data obtained from velocity of sound measurements is available.[18]

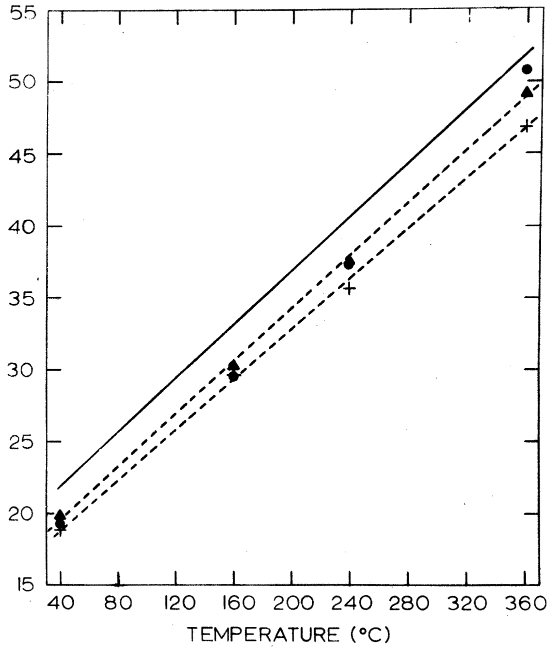

FIG. 1. Temperature dependence of the resistivity of liquid rubidium. The solid line represents experimental data reported in Ref. 2. Points + correspond to calculations made using the structure factor of AL. Points ▲ and ● denote values calculated using structure factors determined from two sets of compressibility data (based on density values of Refs. 10 and 11, respectively).

TABLE III. Experimental and calculated values of the dimensionless coefficient $(T_m/\rho_m)(d\rho/dT)_p$ for liquid rubidium.

	Experimental (data from Ref. 2)	Calculated using $a(k)$ of AL	Calculated using $a(k)$ determined from κ_T data (based on density values of Ref. 10)
$\frac{T_m}{\rho_m}\left(\frac{d\rho}{dT}\right)_p$	1.33	1.46	1.46

For binary systems Eq. (2) must be modified in the following manner:

$$nkT\kappa_T = (1-\eta)^4/[(1+2\eta)^2-\Delta]\,, \qquad (6)$$

where Δ is given by the expression

$$\Delta = \frac{3x(1-x)\eta(1-\alpha)^2}{x+(1-x)\alpha^3} \times \left((2+\eta)(1+\alpha)+3\eta\alpha\,\frac{(1-x)\alpha^2+x}{x+(1-x)\alpha^3}\right). \qquad (7)$$

In Eq. (7) x is the atomic concentration of species 2, $(1-x)$ is the concentration of species 1, and α is the ratio of the hard-sphere radius of species 1 to that of species 2. Ashcroft and Langreth show that, for the Na-K system, α is approximately constant for the whole range of concentration. Furthermore, resistivity calculations show that for the packing parameter it is sufficient to make a linear interpolation,

$$\eta = x\eta_K + (1-x)\eta_{Na}\,,$$

between the value appropriate to pure Na and that of pure K. At 100°C the best fit to resistivity data is given by $\alpha = 0.75$. Using the values $\alpha = 0.75$ and $\alpha = 0.72$, and values of η_K and η_{Na} obtained from compressibility data for the pure metals, the variation of κ_T with composition was calculated from Eq. (6). The calculated and experimental deviation of κ_T at 100°C from a linear extrapolation is shown in Fig. 2. The values calculated from the hard-sphere model exhibit the same shape as the experimental curve, particularly when the ratio of the hard-sphere radii is taken to be 0.72. It should be noted that the deviation, $\delta\kappa_T$, is only a few percent of the total compressibility (values of κ_T range from 18.6 $\times 10^{-12}$ cm^2/dyn for Na to 39.6×10^{-12} cm^2/dyn for K). The error bars shown on the experimental

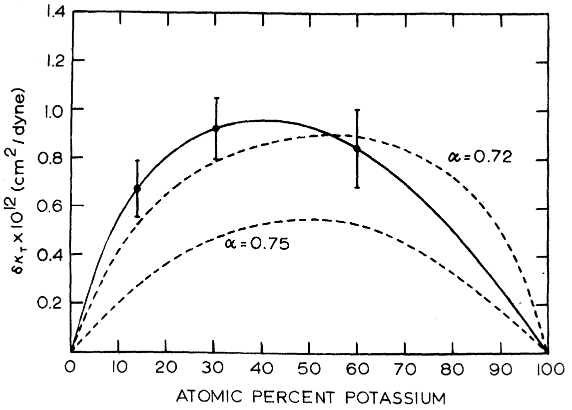

FIG. 2. Experimental (solid line) and calculated (dashed lines) deviations $\delta\kappa_T$ of the isothermal compressibility of sodium-potassium alloys (at 100° C) from a linear extrapolation between the values of κ_T for sodium and potassium.

points in Fig. 2 are based on the following estimates of the accuracy of thermodynamic data [see Eq. (4)] for the Na-K system: $\beta \pm 1\%$, $\rho \pm 0.1\%$, $c \pm 0.1\%$, and $C_p \pm 1\%$. Speed of sound and density measurements are currently in progress in other alkali-metal alloys in order to further test the applicability of Eq. (6) to these systems.

CONCLUSION

The present work provides further experimental evidence supporting the observations of AL that the isothermal compressibility of alkali metals is determined mainly by the repulsive part of the ion-ion potential, and that the net contribution from the long-range ion-ion oscillatory interaction and from the electron gas is small. One important consequence of this is the fact that measurements of κ_T can be used to obtain reliable estimates of the structure factors (up to and including the first peak) of alkali metals and their alloys. The above conclusion is also in agreement with recent theory. The calculations by Ashcroft and Langreth of the ion-ion potential in liquid metals show that the long-range oscillatory interaction is small in the alkali metals. Furthermore, it can be shown that, once exchange and correlation effects are included, the electron gas is very compressible at densities typical of the conduction electrons in alkali metals. Therefore the contribution to κ_T from the electron gas will be small in alkali metals but may be appreciable in polyvalent metals.

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