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ELECTRICAL RESITIVITY OF MOLTEN CESIUM AT HIGH PRESSURES

Eliezer Rapoport
Chemical Physics Group of the National Physical and National Chemical Research Laboratories,
South African Council for Scientific and Industrial Research, Pretoria, South Africa
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Cesium, one of the most interesting substances studied at high pressure, exhibits a $6s$-$5d$ "electron collapse" at the Cs II-III phase transition[1,2] and melting-curve maximum related to it.[3] The resistivity of molten cesium to 45 kbar, recently reported by Jayaraman, Newton, and McDonough,[4] shows a striking increase with pressure in the range 15-40 kbar which was interpreted to be due to the electron collapse taking place continuously in the liquid over a broad pressure range.

Melting curve maxima are now known in the phase diagrams of some 15 elements and inorganic compounds,[5] and Klement[6] suggested that, generally, in such cases the melt consists of two species with a continuous transition to the denser species taking place with increasing pressure. Following this idea, Rapoport[5] recently derived quantitative expressions for the concentration of the two species as a function of pressure and temperature. The purpose of this note is to compare these theoretical equations with the experimental resistivity data of Jayaraman, Newton, and McDonough.[4]

It is postulated that the liquid consists of a mixture of two species $\mathrm{Cs_I}$ and $\mathrm{Cs_{III}}$ (corresponding to the two solid phases, respectively). The mole fraction x of $\mathrm{Cs_{III}}$ is given by the equation

$$\frac{\Delta\mu^0}{kT}=\left(1-\frac{1}{2}z\right)\ln\frac{x}{1-x}+\frac{1}{2}z\ln\frac{\beta-1+2x}{\beta+1-2x}, \qquad (1)$$

where z is the coordination number,

$$\beta=[4(\eta^2-1)x(1-x)+1]^{1/2}, \qquad (2)$$

$$\eta=e^{w/zkT}, \qquad (3)$$

w is the interaction energy between $\mathrm{Cs_I}$ and $\mathrm{Cs_{III}}$, and

$$\Delta\mu^0=\Delta\epsilon^0-T\Delta s^0+p\Delta V^0, \qquad (4)$$

the difference in the chemical potential between $\mathrm{Cs_I}$ and $\mathrm{Cs_{III}}$; these quantities are defined in Ref. 5. Equation (1) was derived by use of the quasichemical approximation.[5,7]

Jayaraman, Newton, and McDonough[4] presented three resistance isotherms at 25, 120, and 220°C. In order to calculate x and $\Delta\mu^0$ values from these data, the following simplifying assumptions are made:

(1) The resistance of liquid Cs is given by

$$R=(1-x)R_{\mathrm{I}}+xR_{\mathrm{III}}. \qquad (5)$$

(2) The parallelism of the 25° and 120° isotherms and the 220°C isotherm below 10 kbar shows that the pressure dependence of R_{I} is essentially temperature independent and is also essentially the same in the solid and liquid phases. This is also borne out in Bridgman's data on the resistance of solid and liquid cesium to 12 kbar.[8] It is also assumed that $R_{\mathrm{III}}-R_{\mathrm{I}}$ is independent of pressure and temperature to the first approximation.

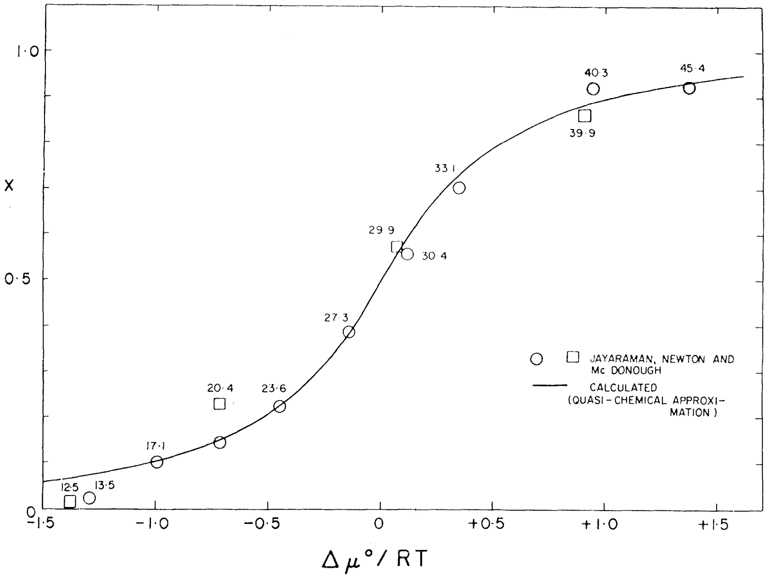

FIG. 1. A plot of Eq. (1) with $w/kT=1.5$ and $z=12$ compared with values computed from the experimental data of Jayaraman, Newton, and McDonough.[4] The numbers denote pressures in kbar.

(3) x is calculated from Jayaraman, Newton, and McDonough's data by the expressions

$$x=(r_{220}-r_{25}-1.75)/9.4$$

where $r=R/R_0$ and

$$(r_{\rm III}-r_{\rm I})_{\rm liquid}=9.4,$$

where allowance has been made for the thermal coefficient of resistivity. The resistivity jump $r_{\rm II}-r_{\rm I}=0.3$ at the Cs I-II transition is included as it is believed that the liquid is partially transformed into Cs$_{\rm II}$.

(4) $\Delta V_{\rm I-III}$ in the liquid is calculated from

$$\begin{aligned}(\Delta V_{\rm I-III})_{\rm liquid}&=(1+\Delta V_{\rm I-liquid}/V)(\Delta V_{\rm I-II}+\Delta V_{\rm II-III})_{\rm solid}\\&=3.42\ {\rm cm}^3/{\rm mole}.\end{aligned}$$

The volume-change data $\Delta V_{\rm I-liquid}=1.81$ cm^3/

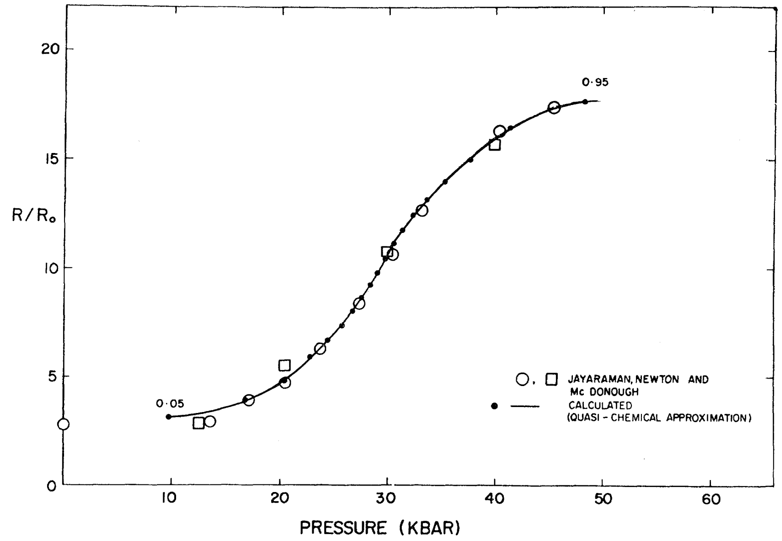

FIG. 2. The 220°C resistivity isotherm of molten cesium. The small closed circles are calculated points at 0.05 increments of x.

mole and $\Delta V_{\text{I-II}}=0.42$ cm^3/mole are taken from Bridgman[8,9] and $\Delta V_{\text{II-III}}=2.91$ cm^3/mole from Hall, Merrill, and Barnett.[2] Then $\Delta\mu^0=3.42\times(p-29.0)$ kbar cm^3. A plot of x vs $\Delta\mu^0/kT$ is presented in Fig. 1. The calculated line is a plot of Eq. (1) with $w/kT=1.50$ and $z=12$ (cubic close-packed, in view of the fact that Cs_{II} and Cs_{III} are fcc[10]). The agreement is indeed striking. The interaction energy w is repulsive and large, and furthermore, w is constant over the entire range 15-45 kbar. This provides an experimental confirmation of the two-species model of Klement and Rapoport.[5] Figure 2 shows the resistivity curve of molten cesium at 220°C calculated from the 25°C resistance isotherm of Jayaraman, Newton, and McDonough and Eq. (1) in excellent agreement with the experimental data.

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[1] P. W. Bridgman, Proc. Am. Acad. Arts Sci. 76, 55 (1948); 81, 167 (1952).

[2] H. T. Hall, L. Merrill, and J. D. Barnett, Science 146, 1297 (1964).

[3] G. C. Kennedy, A. Jayaraman, and R. C. Newton, Phys. Rev. 126, 1363 (1962).

[4] A. Jayaraman, R. C. Newton, and J. M. McDonough, Bull. Am. Phys. Soc. 12, 335 (1967); also Phys. Rev. 159, 527 (1967).

[5] E. Rapoport, J. Chem. Phys. 46, 2891 (1967).

[6] W. Klement, private communication; see also Ref. 5.

[7] The Bragg-Williams approximation yields a simpler equation: $kT\ln[x/(1-x)]+(1-2x)w=\Delta\mu^0$ [Eq. (1a)]. The use of the quasichemical approximation, however, is preferred for $|w|>0.5kT$. A computer program for evaluation of Eqs. (1) and (1a) has been written and tables for various values of w/kT were compiled.

[8] P. W. Bridgman, Proc. Am. Acad. Arts Sci. 60, 385 (1925).

[9] P. W. Bridgman, ibid. 72, 207 (1938).

[10] The coordination number $z=10$ and $w/kT=1.5$ was also tried for Eq. (1). The results are indistinguishable from the line in Fig. 1. The coordination number in liquid Cs at atmospheric pressure is ~9.5. See N. S. Gingrich and L. Heaton, J. Chem. Phys. 34, 873 (1961). The Bragg-Williams approximation (Ref. 7) yields a slightly lower value $w/kT=1.45$, but the actual line obtained is almost identical to the line obtained using the quasichemical approximation.

MOBILITY OF ELECTRONS IN LIQUID He^3 AT THE CRITICAL POINT

I. Modena
Laboratori Nazionali del Comitato Nazionale per l'Energia Nucleare, Frascati, Roma, Italy

and

F. P. Ricci
Istituto di Fisica dell'Università, Roma, Italy
(Received 10 July 1967)

In this Letter we report some experimental results on the mobility of electrons in liquid He^3 at the critical point. Considerable interest[1-3] has been raised recently about the behavior of the transport properties at the critical point. However, as far as diffusion is concerned, very few experimental results[4-6] are available and these are strongly conflicting.

In fact, some authors[4] claim that at the critical liquid-gas point the diffusion coefficient D goes practically to 0, whereas others[6] do not find any peculiar behavior. We chose to measure the mobility of electrons in He^3 since, as is well known, electrons in dense He become practically a rigid bubble[7] of about 14-Å radius, and therefore, they are very useful probes for studying hydrodynamics.[8,9] Moreover, the mobility μ and the diffusion coefficient are related by the Einstein relationship. He^3 is a very convenient substance since it is available at high purity,[10] and very good PVT experimental data are available.[11] On the other hand, quantum effects do not seem to modify qualitatively the critical behavior as has been shown for equilibrium properties.[12] The experimental apparatus is shown in Fig. 1. With the He^4 bath at a temperature of 0.05°K lower than the He^3 temperature, the exchange gas provides any necessary cooling to the He^3 cell, while heating is provided by the resistance heater ⑤ wound around the He^3 cell ④. The heater current is electronically controlled by the two