Electron heat capacity of liquid cesium

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Experimental results on the isochoric heat capacity of liquid cesium are discussed. The free-electron model fails to describe the properties of the conduction electrons of expanded cesium. The possible increase in the electron component of the heat capacity is no greater than 20%.

The properties of liquid cesium at high temperature and pressures have attracted research interest largely because this system presents a real opportunity to experimentally study the evolution of the band structure of a monovalent metal as the interatomic distance changes continuously from solid-state values to gaseous values.

Experiments on the equation of state and the velocity of sound in Ref. 1 revealed that the temperature dependence of the isochoric heat capacity of liquid cesium differs only slightly from that for simple insulating liquids,[2] in which the change in C_v agrees with the known ideas regarding the gradual loss of shear vibrational modes of the atoms of the liquid as it expands.[3] From the standpoint of the usual understanding, the results on C_v (Ref. 1) are quite unexpected, since at high temperatures the heat capacity of the conduction electrons, C_e, predicted by the free-electron model is a substantial component of the heat capacity of the metal, larger than the error in the data on C_v (Ref. 1). In this letter we wish to discuss that result.

Freyland[4] discovered that expanded cesium has some unusual electronic properties: Its (specific) magnetic susceptibility χ increases sharply on the coexistence curve at $T \geqslant 1200$ K (the corresponding densities are $\rho \leqslant 3.3\rho_c$, where ρ_c is the density of the critical point, 0.39 g/cm^3; Ref. 1), reaching a maximum enhancement of a factor of five near the critical point [at $t = [T_c - T)/T_c \approx 3 \times 10^{-2}$, $T_c = 1938$ K; Ref. 1]. The corresponding enhancement factor for the paramagnetic susceptibility of the conduction electrons is approximately three.

Warren *et al.*[5] carried out a detailed study of NMR in liquid cesium from the melting point nearly to the critical point. They measured the Knight shift K and the longitudinal relaxation time of nuclear spins, T_1. They plotted $\eta = [1/T_1]/[1/T_2]_{\text{Korr}}$ and $\xi = |\Psi(0)|_F^2 |\Psi(0)|_A^2$ as functions of the density, where $[1/T_1]_{\text{Korr}} \propto K^2 T$ is the relaxation rate calculated for a gas of free electrons, and $|\Psi(0)|_F^2$ and $|\Psi(0)|_A^2$ are the charge density at the nucleus for electrons at the Fermi level and for the valence electron of the free atom, respectively. It was found that η increases, while ξ decreases, at $\rho \leqslant (3.3 - 3.6)\rho_c$. Warren *et al.*[5] suggest that the data of Refs. 4 and 5 on expanded cesium agree with the model of Brinkmann and Rice.

Even and Freyland[6] studied the Hall effect of saturated liquid cesium at temperatures up to 1600 K. For the Hall coefficient R_H they found that R_H/R_H^f increases monotonically with the temperature, from 1 to 1.2 (here and below, the superscript f signifies the free-electron model).

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Winter *et al.*[7] measured the structure factor of liquid cesium up to the critical point. They used their results and the Ziman formula to calculate the density dependence of the electrical conductivity σ along the saturation line. They found that the calculated values of $\sigma(\rho)$ decrease more slowly than the experimental values at $\rho \leqslant 3.3\rho_c$.

In light of the results of Refs. 4–7, it is obvious that the electron heat capacity of expanded cesium must be different from a free-electron heat capacity. It is equally obvious that C_e should vanish toward the critical point, where a metal–insulator transition occurs (Refs. 1 and 8, for example).

At intermediate densities, on the other hand, the results of these studies are consistent with either an increase or a decrease in the density of states at the Fermi level, $N(E_F)$, in comparison with $[N(E_F)]^f$ and thus the same behavior for C_e/C_e^f.

To illustrate the point, we note that according to the model of Brinkmann and Rice, which was used to interpret the data of Refs. 4 and 5, the increase in χ is proportional to the increase in the effective electron mass $m_e^* = m_e/[1-(\beta U/\beta)^2]$, where U is the Hubbard energy of the intraatomic repulsion of electrons, B is the band width, and β is a constant which approximately 1 (Ref. 9). This relationship leads in turn to the same proportionate increase in $N(E_F)$ and thus $C_e \propto N(E_F)$.

On the basis of the results[5] on ξ described above, however, one could also have the opposite behavior, i.e., a decrease in $N(E_F)$. We could interpret the data on the Hall coefficient[6] in the same spirit. Following Ref. 10, we have $R_H = R_H^f/g$, for this coefficient, where $g = N(E_F)/[N(E_F)]^f$ is the Mott factor. The same comments apply to the results of Ref. 7, since according to the Kubo-Greenwood formula for the conductivity, we would have $\sigma \propto N(E_F)^2$ if the electron mean free path L were comparable to the average interatomic distance a (Ref. 9). For cesium with $\rho \approx 3.3\rho_c$ the data on the electrical conductivity[8] yield $L/a \approx 4$.

The $\chi(\rho)$ dependence of liquid cesium[4] is reminiscent of the corresponding picture for magnetic materials in the initial stage of the approach to an ordered state,[11] with the distinction that the density is playing the role of the temperature. The appearance of spin fluctuations in the process does not terminate in the ferromagnetic or antiferromagnetic order, because of a change in the topology of the electron spectrum of liquid cesium at the transition to the state of a paramagnetic insulator which obeys the Curie law.[5]

Consequently, the data on χ and K evidently do not allow us to draw conclusions about the type of order which the electron subsystem of cesium is approaching—an antiferromagnetic order described by the Brinkmann-Rice model or a ferromagnetic order which would follow from Stoner's model. The observed sign of the deviation from the Korringa relation[5] also fails to qualify as a trustworthy guideline in a search for an answer to this question: An increase in η occurs for ferromagnets and antiferromagnets near the transition because of an increase in spin-fluctuation effects.[12] The results on C_v which we have been discussing, on the other hand, make it difficult to interpret the data of Refs. 4 and 5 on the basis of the Brinkmann-Rice model.

In our opinion, the set of results on the magnetic properties of expanded cesium should be interpreted on the basis of Stoner's model, with spin fluctuations. In that

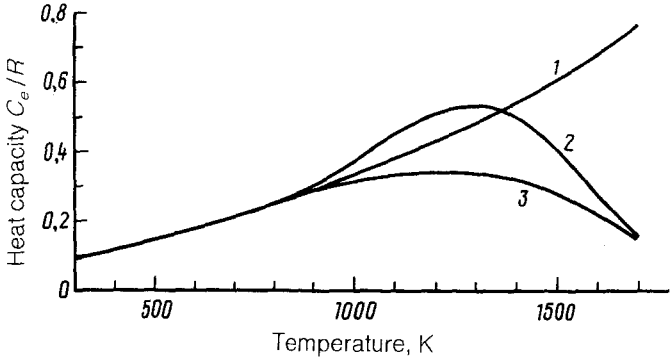

FIG. 1. Electron heat capacity of liquid cesium. *1*—For the free-electron model; *2,3*—possible types of behavior according to the Hubbard model.

model, the increase in the paramagnetic susceptibility is not a result of Fermi electrons exclusively and is not accompanied by a significant increase in C_e (Ref. 9).

According to the Hubbard model, the increase in U/B which occurs with decreasing ρ should lead to a progressive redistribution of the density of states of the half-filled conduction band of the monovalent metal: a decrease in $N(E)$ in the metal and an increase along the edges.[9] In this case the heat capacity C_e would be determined by the position of the Fermi level.

It follows from these arguments that the temperature dependence of C_e along the coexistence curve of liquid cesium might be approximately as shown in Fig. 1 (curves 2 and 3).

Figure 2 shows possibilities for the behavior of the isochoric heat capacity of liquid cesium; these plots incorporate the $C_e(T)$ curves in Fig. 1. The ion component of the heat capacity, $C_i(T)$, was plotted on the basis of the arguments above.

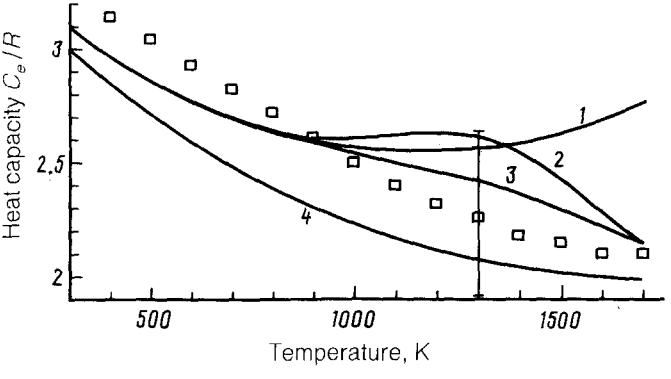

FIG. 2. Isochoric heat capacity of liquid cesium. *1,2,3*—With C_e in accordance with the model estimates in Fig. 1; *4*—ion component of the heat capacity; □—experimental data of Ref. 1.

It can be seen from Fig. 2 that the data on the isochoric heat capacity[1] support the results of Refs. 4–7, which indicate that the free-electron model does not correspond to the real properties of expanded liquid cesium. The possible increase in the electron heat capacity—which we cannot rule out because of the errors in the data of Ref. 1—is small, no more than 20% according to our estimates.

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