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Resistivity of Liquid Sodium-Cesium Alloys up to 300°C

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For a number of liquid sodium-cesium alloys the electrical resistivity ρ has been measured as a function of temperature T in the range 50–300°C. As a function of the cesium concentration c, $(\partial\rho/\partial T)_p$ exhibits a distinct minimum for $c=0.6$, which gradually disappears at higher temperatures. This minimum is related to the results for the resistivity at high pressure recently obtained by Tamaki, Ross, Cusack, and Endo.

Measurements of the electrical resistivity ρ of liquid sodium-cesium alloys as a function of the temperature T have been communicated recently.[1,2] It was demonstrated that, at 100°C, $(\partial\rho/\partial T)_p$, plotted as a function of the atomic concentration c of cesium exhibits a pronounced relative maximum for $c\sim 0.60$. The maximum was ascribed to an ordering phenomenon, more particularly to the formation of a compound Na_3Cs, in the liquid at temperatures close to the melting point. The existence of such a compound was strongly suggested by the results of Kim and Letcher[3] on ultrasonic absorption. This ordering was supposed to disappear gradually at temperatures above the melting point, thus giving rise to a larger value of $(\partial\rho/\partial T)_p$ in that particular temperature range. The maximum was then expected to disappear at higher temperatures.

In order to check this supposition, the measurements were extended towards higher temperatures, and, for some of the alloy compositions, also to lower temperatures. The experimental equipment used for the measurements above 100°C was basically the same as the one described by Hennephof, van der Lugh, and Wright,[4] but the whole system was made of stainless steel. The results are shown in Fig. 1.

Fair agreement with earlier results has been obtained.[5-7] Furthermore, it is evident that it is not the maximum of $(\partial\rho/\partial T)_p$ that disappears at higher temperatures, but rather the minimum: $(\partial p/\partial T)_p$ varies strongly as a function of temperature in this part of the concentration range, whereas for $c<0.25$, $(\partial^2\rho/\partial T^2)_p$ almost vanishes. This is in contradiction with our former supposition.

It is interesting to compare our results on the temperature dependence of ρ with those at high pressure obtained by Tamaki *et al.*[8] for the same alloy system. According to their measurements, $(\partial\rho/\partial p)_T$, plotted as a function of c, changes sign twice. It is negative for $c<0.25$ and for $c>0.80$ (as it is for all pure liquid alkali metals except Li), whereas it is positive for intermediate concentrations. The central composition range for which $(\partial\rho/\partial p)_T>0$ corresponds fairly well to the valley found for $(\partial\rho/\partial T)_p$. The two quantities are related by

$$\left(\frac{\partial\rho}{\partial T}\right)_V=\left(\frac{\partial\rho}{\partial T}\right)_p+\left(\frac{\partial\rho}{\partial p}\right)_T\left(\frac{\partial p}{\partial T}\right)_V. \qquad (1)$$

For the pure alkali metals except Li, $(\partial\rho/\partial T)_V$, $(\partial\rho/\partial T)_p$, and $(\partial p/\partial T)_V$ are positive quantities and $(\partial\rho/\partial p)_T$ is negative.[9-13] Consequently $(\partial\rho/$

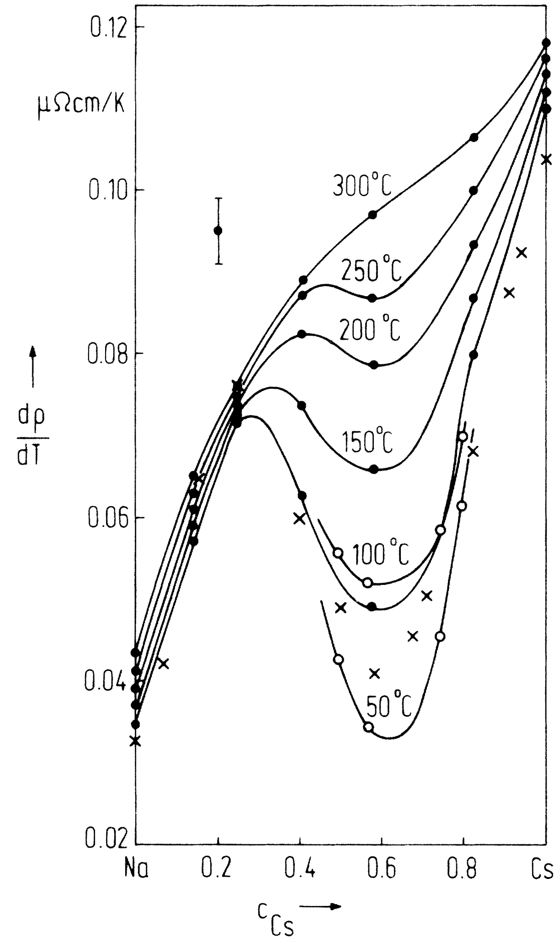

FIG. 1. $(\partial\rho/\partial T)_p$ in sodium-cesium alloys as a function of the cesium concentration. Closed circles, experiment, high temperature series; open circles, experiment, low temperature series; crosses, experiment, Hennephof *et al.* (Ref. 1), see text.

$\partial T)_V < (\partial\rho/\partial T)_p$ and, indeed, experimentally one finds that $(\partial\rho/\partial T)_V/(\partial\rho/\partial T)_p$ is approximately equal to $\frac{2}{3}$.

When discussing the positive values of $(\partial\rho/\partial p)_T$ as found for the central composition range of the Na-Cs system one has to notice, first, that the pressure applied by Tamaki *et al.* (4 kbar) gives rise to a considerable volume change. A temperature of many hundreds of degrees Celsius is required for achieving comparable relative volume changes (but, of course with opposite sign) by heating the metal. Significant changes of the physical properties, particularly $(\partial\rho/\partial p)_T$, have been reported for liquid pure cesium in the pressure interval of 0–4 kbar.[9,10] This makes questionable any quantitative discussion and even the use of differentials in Eq. (1).

Secondly, the values of $(\partial\rho/\partial T)_p$ apply to densities smaller than that at room temperature and pressure, whereas $(\partial\rho/\partial p)_T$ is determined at larger densities. If for $c \sim 0.60$ the measured $(\partial\rho/\partial T)_p$ is fictitiously extrapolated to higher densities (i.e., to temperatures below the melting point), it even becomes negative below, say, 0°C.

By substituting rough estimates of $(\partial p/\partial T)_V$ and $(\partial\rho/\partial p)_T$ in Eq. (1) one can easily demonstrate that the second term in the right-hand side of Eq. (1) counteracts the oscillation in the concentration dependence of $(\partial\rho/\partial T)_p$. One expects $(\partial\rho/\partial T)_V$ to be a flatter function of c than is $(\partial\rho/\partial T)_p$. Furthermore, $(\partial\rho/\partial T)_V$ may exceed $(\partial\rho/\partial T)_p$ considerably in the central part of the composition range, indicating that volume effects play a predominant role. But more detailed measurements of resistivity isobars at smaller intervals of the pressure and at different temperatures as well as reliable values for the compressibility and the thermal expansion coefficient are required for a complete phenomenological description of the resistivity of the concentrated alloys.

Finally, with a view to a possible interpretation in terms of the diffraction model, we want to remark that volume contraction as expected by Christman[14] affects both the d-band scattering and the shape of the structure factor. For this reason we have recently started an investigation of the density of sodium-cesium alloys.

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ally insufficient for a higher order approximation. But for the central part of the Na-Cs composition range it is meaningful to take into account also the curvature of the older ρ-versus-T results. Then the values of $d\rho/dT$ given in Ref. 4 and repeated in Fig. 1 of this paper can be shown to apply effectively to temperatures lower than 100°C, down to 80°C. The discrepancy for pure cesium cannot be explained in this way.

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Nonlocal Exchange and Correlation Effects on the Fermi Surface of Metals*

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The inhomogeneous-electron-gas theory of Hohenberg, Kohn, and Sham has been used to investigate the effects of nonlocal exchange and correlation on the Fermi surface of a simple cubic metal. The periodic lattice effects were represented by a realistic simple model pseudopotential. We find that the nonlocal terms substantially reduce the maximum Fermi-surface distortions, as experiments suggest.

Comparisons of experimental Fermi-surface (FS) distortions with first-principles calculations of these distortions result in significant discrepancies. A particularly striking example is the recent work of Janak, Williams, and Moruzzi,[1] who examined the effect of local exchange and correlation potentials on the FS of Cu. None of the potentials based on fundamental theory (Slater,[2] Kohn and Sham,[3] and Hedin and Lundqvist[4]) resulted in agreement with experiment. It is especially disappointing that the local potential of Hedin and Lundqvist[4] leads to no improvement over the simple local theory.[3]

There have been numerous calculations of the band structures and Fermi surfaces of the alkali metals. (For a recent review see Lee.[5]) The general tendency is for the theory to produce maximum distortions which are considerably larger than those observed. For example, Lawrence[6] found that the FS of Cs touched the zone boundary in the (1, 1, 0) direction. Other workers[5] have found maximum distortions of order a factor 2 too large. In Li the maximum calculated distortions[5] are again a factor 2 larger than the most recent experimental value.[7] All the above first-principles calculations share one common approximation: They calculate the FS with a local exchange-correlation potential. Kane[8] has recently investigated the effects of nonlocal exchange and correlation in the band structure of Si and found them to be substantial.

The primary objective of this work is to show by direct calculation with a realistic model that the FS given by a nonlocal many-body-type theory is significantly different than the corresponding local theory, both treated within the framework of the Hohenberg-Kohn-Sham[3,9,10] theory of an inhomogeneous electron gas.

The general equation from which elementary excitations E_k of quasiparticles, and hence the corresponding FS, can be determined is[10]

$$(\hbar^2/2m)\nabla^2\psi_{\vec{k}}(\vec{r}) + \int d^3r'\, \Sigma(\vec{r}, \vec{r}\,'; E_{\vec{k}})\psi_{\vec{k}}(\vec{r}\,') = E_{\vec{k}}\psi_{\vec{k}}(\vec{r}), \tag{1}$$

where Σ is the so-called mass operator. To exhibit explicitly the local and nonlocal components of Σ, write

$$\Sigma(\vec{r}, \vec{r}\,'; E) = V(\vec{r})\,\delta(\vec{r} - \vec{r}\,') + M(\vec{r}, \vec{r}\,'; E), \tag{2}$$

where $V(\vec{r}) = V_{\text{ext}}(\vec{r}) + V_{\text{H}}(\vec{r})$, $V_{\text{ext}}(\vec{r})$ is the applied external potential, $V_{\text{H}}(\vec{r})$ is the electrostatic potential (Hartree field) of the electrons, and M is the nonlocal (exchange and correlation) part of Σ