'ELECTRON COLLAPSE' AND THE RESISTIVITY OF LIQUID CESIUM

T.G. RAMESH and S. RAMASESHAN
Materials Science Division, National Aeronautical Laboratory, Bangalore-17, India

Received 27 March 1972

The electron collapse in cesium is pictured as the formation of a 'virtual bound state', the tunneling process accounting for the 6s-5d dynamic conversion. The anomalous variation of the resistivity of liquid cesium with pressure has been explained satisfactorily.

Cesium exhibits an iso-structural phase transition at 42.5 kbar which has been attributed to the 6s-5d 'electron collapse' [1]. It also exhibits a double maximum in the fusion curve [2] which implies a rapid variation in the density of liquid Cs with pressure, the liquid eventually attaining a density higher relative to the solid f.c.c. structure. Taking these along with their measurements on the variation of the resistivity of liquid Cs with pressure, Jayaraman et al. [3] postulated that the electron collapse in the liquid phase is continuous and occurs over a broad pressure region.

In this note, it is suggested that the 6s-5d electron collapse results in the formation of a 'virtual bound state' accompanied by d-wave scattering resonance. Numerical calculations based on this postulate explains the variation in the resistivity of liquid Cs with pressure lending strong support to the 'two-species' model [4].

In our 'two-species' model, we choose the nearest neighbour distance of cesium atoms in the collapsed f.c.c. phase [5] as an empirical criterion for the electron collapse. Over short ranges, such a critical interatomic distance would be favoured in the liquid accompanied by electron collapse even at very much lower pressures. The increasing of pressure enhances the concentration of the collapsed species. In cesium, the empty 5d band above the Fermi level is lowered as the interatomic distance decreases, ultimately merging with the conduction band. When the electron collapse occurs, the electron is held in the region of the potential by the centrifugal barrier term $l(l+1)/\gamma^2$ resulting in the formation of a 'virtual bound state' whose life time is finite. The electron therefore tunnels out of the potential well and the collapsed Cs atom reverts back to its normal form. This dynamic conversion is a new feature of our model. Since the 5d state is more localised than the 6s state, the collapsed Cs atom has a smaller atomic volume.

Fig. 1. The form factor $V_o(X)$ for normal cesium. The resonant form factor $V'_d(X)$ when $E_d - E = \frac{1}{2}\Gamma$, a special case wherein $V'_d(X) = V'_d(X)$.

The postulate of the formation of a 'virtual bound state' is equivalent to the d-wave component of the scattering amplitude passing through a resonance. Using the phase shift formalism elucidated in ref. [6], we have for the d-wave form factor

$$U_d = -\frac{2\pi\hbar^2}{m\Omega_o}\cdot\frac{5}{k}\cdot P_2(\cos\theta)\cdot\frac{\Gamma}{2(E_d-E)-i\Gamma} \qquad (1)$$

where Γ represents the width of the d-wave resonance and θ, the scattering angle. The d-wave form factor is

Fig. 2. ρ/ρ_0 versus P diagram (ρ_0 = resistivity at 25° C and atmospheric pressure).

complex and its imaginary component cannot be ignored, especially near resonance. The decrease in the positive energy of the 5d state as the interatomic distance approaches a critical value has the effect of increasing the life time of the virtual bound state. The electron-ion interaction corresponding to the normal species (A species) can be described by a potential scattering amplitude. The A species and the collapsed B species are characterised by the screened form factors (using Hartree's dielectric function) given by

$$V_A = V_o \text{ and } V_B = V_o + V_d' + V_d'' \,. \qquad (2)$$

Here V_d' and V_d'' are the real and the imaginary components of the screened d-form factor which are obtained using the resonance formula given by eq. (1). Fig. 1 presents the variation of V_d'' with $X(=\sin^2\frac{1}{2}\theta)$ for a typical value of $E_d - E = \frac{1}{2}\Gamma$. Also shown in the diagram is V_o where the off resonance contribution to the form factor is taken into account [7]. The sudden dip in V_d'' near $X \approx 1$, corresponding to back scattering of the Fermi sphere is an important feature of d-wave resonance.

The basic Ziman formula [8] for the resistivity of a liquid metal has been modified for a 'two species' system when one of the species possesses a complex form factor using the formulation in [9]. The resistivity appropriate to our 'two species' system is given by

$$\rho = \frac{12\pi\Omega_o}{e^2\hbar v_F^2} \int_0^1 Z X^3 \mathrm{d}X \qquad (3)$$

where

$$Z = CS_{BB}(X)V_B(X)V_B^*(X) + (1-C)S_{AA}(X)V_A^2(X) + 2\sqrt{C(1-C)}S_{AB}(X)V_A(X)\{V_o(X) + V_d'(X)\}\,.$$

The concentration C of the collapsed species at various pressures have been obtained from a thermodynamic analysis [10]. In the absence of experimental data, the partial structure factors (S_{AA}, S_{BB} and S_{AB}) have been evaluated using the Percus-Yevick expressions for the hard sphere binary liquid mixtures [11]. The packing fraction η, at each pressure is chosen such that the long wavelength limit of the structure factor given by the compressibility formula [11] is satisfied. The variation of the Fermi wave number, k_F, with volume has been taken into account using the free electron formula. In our simplified model, the variation of the form factors with volume has not been taken into account.

Most of the salient features of the experimental curve (fig. 2) find satisfactory explanation. (i) The shallow resistivity minimum observed in the low pressure region: Since the concentration of the collapsed species is small, the liquid can be considered as a one component system. The isothermal compressibility decreases with increase of pressure so that the long wavelength limit of the structure factor, $S_{AA}(0)$, also decreases with pressure. The contribution to the resistivity integral from the region of lower values of X ('plasma resistance') decreases with increase of pressure. On the other hand, the 'structural resistance' increases as the upper limit of integration samples region of higher values of $S_{AA}(X)$. The shallow resistivity minimum is due to the slight preponderance of the former over the latter effect. (ii) The rapid variation of the resistivity in the 20 to 40 kbar region: This is due to the increasing concentration of the collapsed species. The strong dip in V_d' and V_d'' near $X \approx 1$ (the region of high weightage in the resistivity integrand) shows that the collapsed species contribute significantly towards the resistivity. (iii) Saturation above 45 kbar: This is essentially due to the electron collapse being nearly complete. Fig. 2 presents the theoretically cal-

culated curves for two values $E_d - E = 0$ and $E_d - E = \frac{1}{2}\Gamma$. It can be seen that both these curves have the same general features as that of the experimental curve. Our simplified model, in spite of various approximations, provides a satisfactory explanation to all the experimental results.

Our grateful thanks are due to Dr. A. Jayaraman for introducing us to this problem.

References

[1] R. Sternheimer, Phys. Rev. 78 (1950) 235.
[2] G.C. Kennedy, A. Jayaraman and R.C. Newton, Phys. Rev. 126 (1962) 1363.
[3] A. Jayaraman, R.C. Newton and J.M. McDonough, Phys. Rev. 159 (1967) 527.
[4] Referred to by E. Rapapport in ref. [10].
[5] H.T. Hall, L. Merrill and J.D. Barnett, Science 146 (1964) 1297.
[6] J.M. Ziman, Adv. Phys. 13 (1964) 89.
[7] V. Bortolani and C. Calandra, Phys. Rev. 1B (1970) 2405.
[8] J.M. Ziman, Phil. Mag. 6 (1961) 1013.
[9] T.G. Ramesh and S. Ramaseshan, J. Phys. C. (Solid State) 4 (1971) 3029.
[10] E. Rapapport, J. Chem. Phys. 48 (1968) 1433.
[11] N.W. Ashcroft and D.C. Langreth, Phys. Rev. 156 (1967) 685.