

## High pressure behaviour of liquid caesium

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**Abstract.** This paper deals with the anomalous behaviour of liquid caesium at high pressures. A model for the phenomenon of electron collapse in the liquid phase, based on the anomalous density variation of liquid caesium with pressure has been proposed. The process of  $6s \rightarrow 5d$  electron collapse is pictured as the formation of a virtual bound state and the tunnelling process accounts for the  $6s \rightleftharpoons 5d$  dynamic conversion. The same model together with the Friedel sum rule has been used to explain the resistivity variation of liquid caesium with pressure. The resistivity minimum observed in most of the liquid alkali metals in the low pressure region has been explained. The agreement with the experimental curve is good in the low pressure region whereas a large discrepancy exists at higher pressures. This may be due to the breakdown of the Ziman's resistivity formula under conditions of resonance scattering.

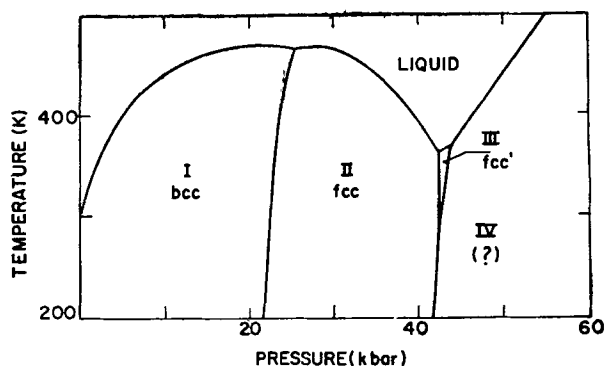
**Keywords.** Liquid caesium; electron collapse; resonance scattering; resistivity

### 1. Introduction

The high pressure behaviour of caesium has been a subject of numerous investigations. The main interest in this substance is centered round the existence of a double maximum in the fusion curve, first established by Kennedy *et al* (1962) and a later discovery of an iso-structural phase transition near 42 kbar pressure (Hall *et al* 1964). Jayaraman *et al* (1967) and later McWhan and Stevens (1969) have made a more detailed study of the phase diagram of caesium upto 50 kbar pressure.

Figure 1 shows the phase diagram of caesium given by McWhan and Stevens (1969). At 23 kbar pressure, there is a phase transition involving bcc to fcc transformation. However, at 42.5 kbar, there is another first order phase transition involving the so-called  $6s$ - $5d$  electron collapse (Sternheimer 1950). Hall *et al* (1964) through their high pressure x-ray diffraction work established that this phase transition is iso-structural and also measured the lattice parameter decrease accompanying the transition.

The main feature of the phase diagram is the existence of a double maximum in the melting curve. The application of the Clausius-Clapeyron equation,  $dT/dP = \Delta V/\Delta S$ , to the melting process leads to the result that at the maxima, the density of liquid caesium is equal to that of the solid phase lying below the corresponding maxima. The negative slopes following the two maxima in the fusion curve imply that the density of the liquid phase is higher than that of the corresponding solid phase. The increase in density immediately after the first maximum can, in principle, be understood as arising due to an increase in the co-ordination number in the liquid phase relative to the bcc co-ordination. However, this kind of reasoning fails to account



**Figure 1.** Phase diagram of caesium (McWhan & Stevens 1969).

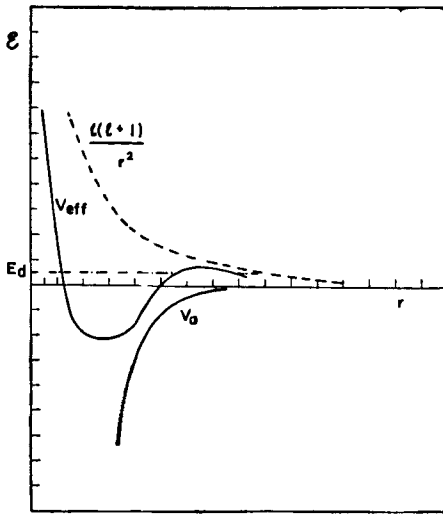
for the density variation in the region following the second maximum, as the solid phase underneath is in the closest packed configuration. *This anomalous variation in the density of liquid caesium with pressure, i.e. the liquid becoming denser than the closest packed solid phase, is perhaps the most interesting feature of this substance.* Jayaraman *et al* (1967), based on their resistance data on liquid caesium obtained as a function of pressure upto 50 kbar, postulated that the electron collapse occurs in the liquid phase over a broad pressure range, in contrast to the solid phase where this phenomenon takes place at 42.5 kbar pressure.

The present investigation was undertaken to provide a model for the phenomenon of 'electron collapse' in the liquid phase and also to seek an explanation for its resistivity behaviour under pressure. It is proposed that the 6s-5d electron collapse results in the formation of a 'virtual bound state' accompanied by d-wave scattering resonance (Ramaseshan 1972, Ramesh and Ramaseshan 1972). Numerical calculations based on this postulate generally explains all the main features of the experimental resistivity versus pressure data. However, the large discrepancy between the experimental and the theoretically derived resistivity values in the high pressure region (30 to 40 kbar) is shown to be mainly due to the breakdown of Ziman's resistivity formula rather than that of the basic model itself.

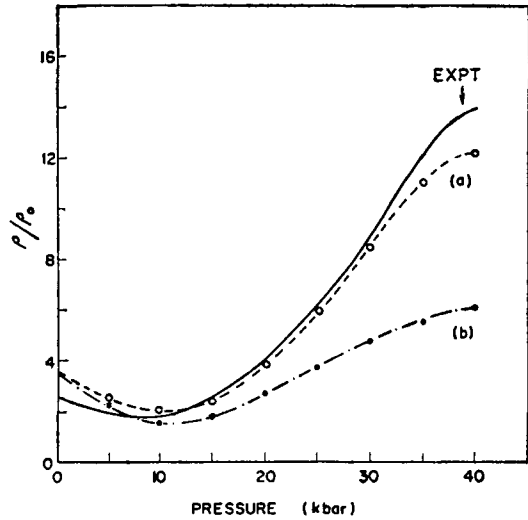
## 2. Two species model

We shall briefly go into the so called 'two species' model of liquid caesium. Klement pointed out that the negative slope of the fusion curve in the region lying after the second maximum, implies that the phenomenon of electron collapse occurs in the liquid phase at much lower pressures. Following this suggestion of Klement, Rapaport (1968) developed the 'two-species' model from a thermodynamic point of view and obtained the concentration of the collapsed species at various pressures using the resistance data of Jayaraman *et al* (1967).

The two-species model that we have employed to explain the experimental results of Jayaraman *et al* (1967) needs explanation. We choose the nearest neighbour distance exhibited by caesium atoms in the collapsed fcc phase as an empirical criterion for the occurrence of electron collapse in the liquid phase. When such a configuration is realised, the empty 5d band which normally lies above the 6s conduction band, would be lowered due to the enhancement in the d-orbital overlap. The 6s-5d electron collapse can then be pictured as the formation of a virtual bound state. The electron is held in the region of the potential by the centrifugal barrier potential



**Figure 2.** Schematic diagram showing the effect of adding the centrifugal barrier potential  $l(l+1)/r^2$  to the atomic potential  $V_a$  to give rise to an effective potential  $V_{eff}$ . The position of the resonance level  $E_d$  is also shown.



**Figure 3.** Resistivity vs pressure diagram for liquid caesium. The experimental curve from Jayaraman *et al* (1967) compared with the theoretical prediction. Curve a corresponds to the choice  $E_d - E = \Gamma/2$  used in evaluating the resonant d-wave form factor. Curve b corresponds to the resistivity data computed using the Friedel Sum rule.

$l(l+1)/r^2$ . This is schematically represented in figure 2. However the lifetime of an electron in the virtual bound state is finite so that when it tunnels out of the potential well, the collapsed caesium atom reverts back to its normal form. This  $6s \rightleftharpoons 5d$  dynamic conversion is a new feature of our model. The collapsed species have a smaller atomic volume as the 5d state is more localised than the 6s state. We note that a virtual bound state can indeed be more localised than a real bound state (Anderson 1967).

In support of the two species model, we emphasise that the inhomogeneities present in the liquid phase favour the creation of the collapsed species at a very much lower pressure. This conclusion is based on the general thermodynamic result relating the relative fluctuation in the number density in a volume element  $V$  to the isothermal compressibility, viz.

$$\langle (N - \bar{N})^2 / \bar{N}^2 \rangle = kT\chi_T/V \quad (1)$$

Here  $\bar{N}$  represents the mean number density and  $\chi_T$ , the isothermal compressibility. The high compressibility of liquid caesium together with  $T \approx 500$  K imply the existence of large density fluctuations in the system. In this connection mention should be made of the work of Yoshida and Kamakura (1973) who have shown that a maximum in the melting curve can occur owing to the softness of the repulsive potential. These two facts taken together suggest that over short ranges, a critical interatomic distance would be favoured in the liquid phase accompanied by  $6s \rightarrow 5d$  electron collapse. The increase of pressure facilitates the occurrence of such a configuration, thereby increasing the concentration of the collapsed species.

### 3. Resistivity variation with pressure

Figure 3 shows the relative resistivity *versus* pressure curve (Jayaraman *et al* 1967) for liquid caesium at 220°C. The salient features of this curve include the resistivity minimum observed in the low pressure region, the rapid increase in the resistivity in the 20-40 kbar region, and a general flattening above 40 kbar pressure.

### 4. Electron-ion scattering amplitude

The phenomenon of resonance scattering is well known (Messiah 1965). In our present model we assume that when the special interatomic distance is favoured in the liquid phase, an electron possessing the 6s character is resonantly scattered to the 5d state. As remarked in the earlier section, the caesium ion together with the conduction electron in a virtual bound state forms what may be termed the 'collapsed species.' The formation of a virtual bound state as the 5d band approaches the 6s conduction band is equivalent to the d-wave component of the scattering amplitude passing through a resonance. The d-wave scattering amplitude is given by the partial wave formula (Messiah 1965),

$$f_d(E, \theta) = \frac{2l+1}{k} P_l(\cos \theta) \exp [i\delta_l(E)] \sin \delta_l(E) \quad (2)$$

Here  $\delta_l(E)$  represents the phase shift associated with the  $l^{\text{th}}$  partial wave and is of prime importance in evaluating the scattering amplitude. The Legendre polynomial  $P_l(\cos \theta)$  describes the angular variation of the scattering amplitude. The behaviour of the phase shift  $\delta_l$  near the resonance energy level  $E_d$  is well described by the formula

$$\tan \delta_l = \Gamma / 2(E_d - E) \quad (3)$$

Here  $\Gamma$  represents the half-width of the d-wave resonance. Under conditions of resonance the formula for the d-wave scattering amplitude reduces to the well-known Breit-Wigner relation

$$f_d(E, \theta) = \frac{2l+1}{k} P_l(\cos \theta) \frac{\Gamma}{2(E_d - E) - i\Gamma} \quad (4)$$

The scattering amplitude associated with all the other partial waves is represented by  $f_0$  and this approximately describes the electron-normal species interaction. Thus the normal species (referred to as A species) and the collapsed B species are characterised by the scattering amplitudes

$$\text{and } \left. \begin{array}{l} f_A = f_0 \\ f_B = f_0 + f'_d + if''_d \end{array} \right\} \quad (5)$$

Here  $f'_d$  and  $f''_d$  correspond to the real and the imaginary parts of the d-wave scattering amplitude given by relation (4). The notation is similar to that used in the anomalous scattering of x-rays or neutrons (Ramesh and Ramaseshan 1971). It is clear from the relation (5) that the scattering amplitude associated with the collapsed species is essentially complex. The physical significance of the imaginary component of the scattering amplitude is contained in the optical theorem where  $f''_d(0)$  is related to the total scattering cross-section by Eq. (6)

$$\sigma = \frac{4\pi}{k} f''_d(0) \quad (6)$$

We may note here that even  $f_0$  is associated with an imaginary component of a much smaller magnitude which is omitted. To obtain the electron-ion form factor from the scattering amplitude, we use the  $t$ -matrix formulation (Ziman 1969). The bare ion d-wave form factor in this approach is given by

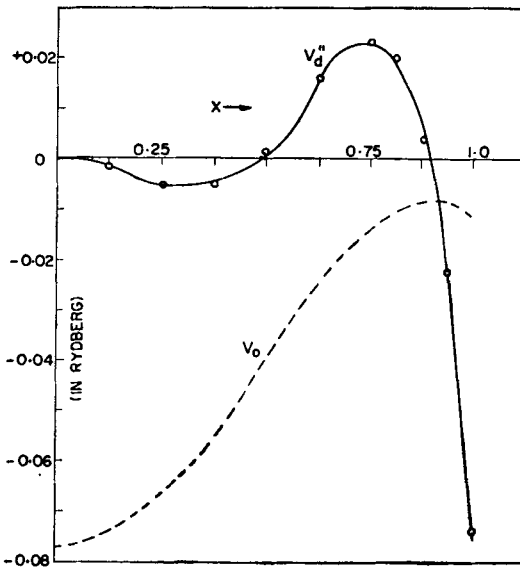
$$U_d(E, \theta) = -\frac{2\pi\hbar^2}{m\Omega_0} f_d(E, \theta) \quad (7)$$

where  $\Omega_0$  represents the atomic volume. These form factors are then screened using the Hartree static dielectric function  $\epsilon(X)$  given by the relation

$$\epsilon(X) = 1 + \frac{\lambda^2}{X^2} \left\{ \frac{1}{2} + \frac{1+X^2}{4X} \log \left| \frac{1+X}{1-X} \right| \right\} \quad (8)$$

where  $\lambda^2 = (\pi a_0 k)^{-1}$  and  $X = \sin \theta/2$ ,  $\theta$  being the scattering angle. Thus  $V_0$ ,  $V_d'$  and  $V_d''$  represent the screened form factors associated with  $f_0$ ,  $f_d'$  and  $f_d''$  respectively.

It is clear from relation (4) that calculation of the d-wave scattering amplitude requires a knowledge of the two parameters and  $E_d = E$ . We have chosen for  $\Gamma$  a value of 0.1 Ry in conformity with Ham's band structure calculations (Ham 1962). For the present discussion we treat  $E_d - E$  as an adjustable parameter though in a later section a more appropriate procedure for obtaining the scattering amplitude is discussed. Figure 4 shows the variation of  $V_d''$  with  $X$  ( $= \sin \theta/2$ ) obtained by assuming  $E_d - E = \Gamma/2$ . For this particular choice of  $E_d - E$ , the screened form factors  $V_d'$  and  $V_d''$  are identical except for a phase difference of  $\pi/2$  between them.



**Figure 4.** The screened form factor  $V_0(x)$  for normal species from Bortolani and Calandra (1970). The resonant form factor  $V_d''(x)$  when  $E_d - E = \Gamma/2$ , a special case wherein  $V_d'(x) = V_d''(x)$ .

The sudden dip in  $V_d''$  near  $X \simeq 1$ , corresponding to back scattering on the Fermi surface is the main feature of the d-wave resonance. The form factor  $V_0$  in figure 4 is taken from the work of Bortolani and Calandra (1970) where even the off resonance contribution to the form factor has been taken into account.

### 5. Resistivity of a two-species system

The resistivity of a monoatomic liquid metal, according to Ziman's theory (Ziman 1964) is given by

$$\rho = \frac{12\pi\Omega_0}{e^2\hbar v_F} \int_0^1 S(X)V(X)^2 X^3 dX \quad (9)$$

where  $S(X)$  and  $V(X)$  represent the structure factor and the form factor respectively. This basic formula has been modified for a two-species system when one of the species possesses a complex form factor (Ramesh and Ramaseshan 1971). The resistivity formula appropriate to our 'two-species' system is given by

$$\rho = \frac{12\pi\Omega_0}{e^2\hbar v_F} \int_0^1 Z X^3 dX \quad (10)$$

where

$$Z = CS_{BB}(X)V_B(X)V_B^*(X) + (1-C)S_{AA}(X)V_A^*(X) \\ + 2[C(1-C)]^{1/2} S_{AB}(X)V_A(X)\{V_0(X) + V_d'(X)\}$$

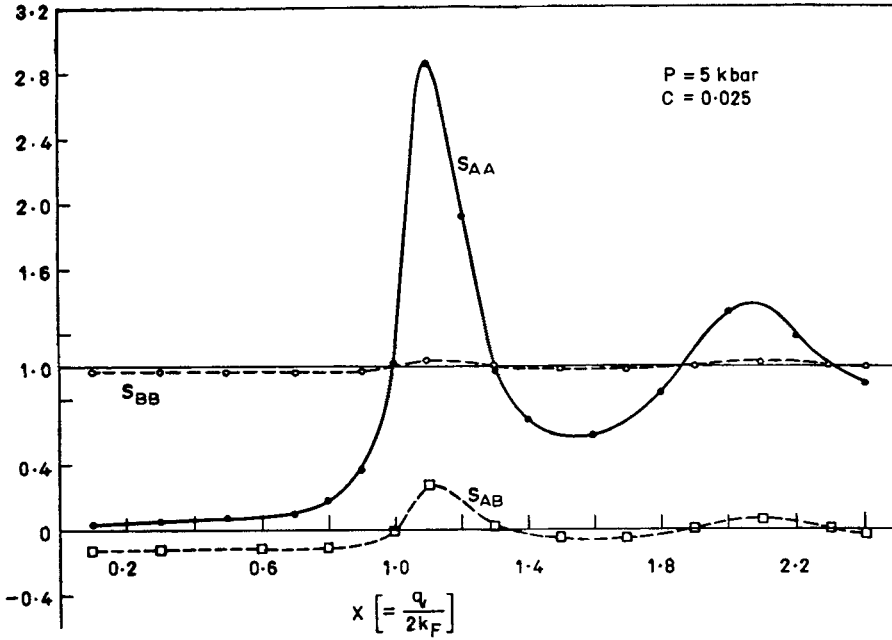
Here  $C$  represents the concentration of the collapsed species.  $S_{AA}(X)$ ,  $S_{BB}(X)$  and  $S_{AB}(X)$  represent the partial structure factors of the system corresponding to  $A-A$ ,  $B-B$  and  $A-B$  interaction. The presence of the weightage factor  $X^3$  in the integrand emphasises that the region  $X \simeq 1$  corresponding to back scattering on the Fermi surface makes a significant contribution to the resistivity.

It is evident from the relation (6) that a calculation of the resistivity of a two-species system requires a knowledge of the partial structure factors, the concentration of the collapsed species at a given pressure and the form factors. The partial structure factors of a binary system can, in principle, be obtained experimentally using special techniques (Ramesh and Ramaseshan 1971). However it is unlikely that these methods can be utilised in the case of liquid caesium, for the x-ray form factors would be nearly the same for both the normal and the collapsed species. In view of these experimental difficulties, we take recourse to an analytical approach, viz. the Percus-Yevick (PY) theory of binary liquid mixtures, to obtain the partial structure factors of liquid caesium at various pressures. Detailed expressions for the partial structure factors were given by Ashcroft and Langreth (1967). The parameters involved in these expressions are the packing fraction  $\eta$ , the concentration of the collapsed species  $C$ , and  $a$ , the ratio of the hard sphere diameters of the two species. The concentration of the collapsed species at various pressures has been obtained by Rapaport (1968) from a thermodynamic analysis and we use this data in our work. The hard sphere diameter of the normal species was chosen to be the one which best describes the structure factor at 30°C. The high pressure x-ray diffraction work of Hall *et al* (1964) is used to estimate the hard sphere diameter of the collapsed species. The packing fraction which is a function of pressure can then be determined using the relation that exists between the long wavelength limit of the structure factor given by the Ornstein-Zernicke compressibility formula and the Percus-Yevick theory of binary liquid mixtures (Ashcroft and Langreth 1967), viz.

$$S(0) = \frac{kT}{\Omega_0} \chi_T = (1-\eta)^4 \{(1+2\eta)^2 - \Delta\}^{-1} \quad (11)$$

where

$$\Delta = \frac{3\eta(1-a)^2 C(1-C)}{(1-C) + Ca^3} \left\{ (2+\eta)(1+a) + \frac{3\eta a(1-C+Ca^2)}{(1-C) + Ca^3} \right\}$$



**Figure 5.** Partial structure factors of a binary system of normal and collapsed atoms of caesium.

The isothermal compressibility,  $\chi_T$ , was evaluated at various pressures using the specific volume *versus* pressure graph of liquid caesium given by Kennedy *et al* (1962). The parameters  $\eta$ ,  $c$  and  $a$  (which are essentially fixed using experimental data) are sufficient to evaluate the partial structure factors of the system. Figure 5 shows a typical set of partial structure factors calculated from the PY theory for a particular value of  $C=0.025$ . Since the concentration of the collapsed species is very small, the partial structure factor  $S_{BB}(X)$  is close to unity throughout, signifying the random arrangement of the collapsed species. The partial structure factor  $S_{AB}(X)$  describing the unlike species interaction oscillates about zero and negative in the low  $X$  region. This behaviour is due to a particular choice in the definition of the partial structure factor, *viz.*

$$S_{\alpha\beta}(X) = \delta_{\alpha\beta} + (C_\alpha C_\beta)^{\frac{1}{2}} \int_0^\infty [g_{\alpha\beta} - 1] \frac{\sin kr}{kr} 4\pi r^2 dr \quad (12)$$

In calculating the resistivity as a function of pressure, one has to consider the effect of the volume contraction on (a) the radius  $k_F$  of the Fermi sphere, (b) the partial structure factors, and (c) the form factors appropriate to the normal and the collapsed species.

The variation in the radius of the Fermi sphere with pressure has been taken into account using the free electron formula

$$k_F^3 = 3\pi^2 n \quad (13)$$

where  $n$  represents the number density of electrons. The partial structure factors at each pressure can be evaluated using an appropriate choice of the parameters  $\eta$ ,  $C$  and  $a$  as described in the last section. The effect of pressure on the form factors is neglected in our simplified model. However this approximation is justified as the large

enhancement in the resistivity with pressure is mainly due to the increase in the concentration of the collapsed species.

## 6. Results and discussion

The resistivity of liquid caesium evaluated as a function of pressure is given in figure 3. Curve a corresponds to the choice  $E_d - E = \Gamma/2$  used in evaluating the d-wave form factor. Curve b represents the resistivity data computed from the d-wave phase shift  $\delta_2(E_F)$  which is estimated using the Friedel sum rule (Friedel 1954). The values of the parameters used in the calculation are summarized in table 1.

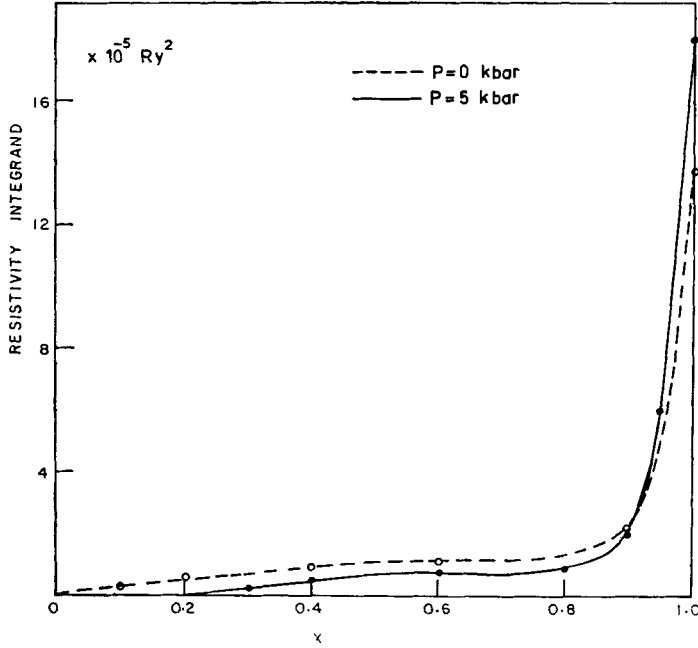
**Table 1.** Values of the parameters used in the calculation of the resistivity of liquid caesium (see figure 3)

Pressure in kbar	$\eta$	$C$	$\alpha$
0	0.4504	0	1
5	0.4874	0.025	0.961
10	0.5112	0.05	0.961
20	0.5220	0.2	0.961
30	0.5234	0.55	0.961
40	0.5424	0.90	0.961

### 6.1. Resistivity minimum in the low pressure region

The resistivity minimum observed in the low pressure region is a general feature of the alkali metals (except lithium) both in the solid and liquid phase and was first observed by Bridgman (1949). In the solid phase the initial decrease in the resistivity is connected with the change in the lattice vibrational spectrum with volume and is governed by the Gruneisen-Bloch equation. However, the same behaviour observed in the liquid phase has not been explained so far. The present investigation provides a simple explanation for this behaviour. We shall treat here only the case of liquid caesium though the argument holds good for the other liquid alkali metals as well. In the low pressure region the concentration of the collapsed species is so small that for all qualitative reasoning we can treat the liquid as a one-component system. The initial decrease in the isothermal compressibility with pressure causes the long wavelength limit of the structure factor  $S_{AA}(0)$  to decrease in accordance with the Ornstein-Zernicke compressibility formula. Thus the contribution to the resistivity integral from the region of small momentum transfer called the plasma resistance decreases with increase of pressure. On the other hand, the increase in  $k_F$  with pressure causes the upper limit of integration in the resistivity formula to sample regions of higher values of  $S_{AA}(X)$  so that the structural resistance increases with pressures. Further the existence of the collapsed species though in a small concentration has the effect of increasing the structural resistance due to their large form factor in the region  $X \simeq 1$ . However the former effect i.e. the decrease in the plasma resistance slightly predominates over the latter leading to a shallow minimum in the resistivity of liquid caesium at about 8 kbar pressure. In other alkali metals the resistivity minimum is more pronounced due to the absence of the collapsed species. Figure 6 shows the resistivity integrand evaluated as a function of  $X$  for two pressures, viz.  $P=0$  and 5 kbar. The two opposite effects in the region of small and large values of  $X$  can be clearly seen in the diagram.





**Figure 6.** Resistivity integrand as a function of  $x$  ( $=\sin \frac{\theta}{2}$ ) at two pressures viz.,  $P=0$  and  $P=5$  kbar.

### 6.2. Steep resistivity variation in the 20-40 kbar region

The large variation of the resistivity in the 20 to 40 kbar region 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 (resonant scatterers) contribute significantly to the resistivity. The theoretically calculated resistivity curve obtained by choosing  $E_d - E = \Gamma/2$  is in close agreement with the experimental curve.

As remarked previously the central quantity involved in evaluating the d-wave scattering amplitude is  $\delta_2(E)$ , the phase shift of the  $l=2$  partial wave. Though two parameters  $\Gamma$  and  $E_d - E$  are involved in the Breit-Wigner formula, it is important to notice that knowledge of just  $\delta_2$  alone, evaluated at the Fermi energy, is sufficient to arrive at the appropriate form factor. Further, an estimate of  $\delta_2$  can be made using the Friedel sum rule, viz.

$$\mathcal{Z} = \frac{2}{\pi} \sum_l (2l+1) \delta_l(E_F) \quad (14)$$

where  $\mathcal{Z}$  represents the screening charge around each of the ions in the liquid. While applying this relation to the system of interest, one could make the reasonable assumption that  $\delta_2$  contributes most to the screening charge around the collapsed atom. Putting  $\mathcal{Z}=1$  (caesium being monovalent) we get  $\delta_2(E_F) \approx \pi/10$ . It is clear from relation (3) that choosing  $E_d - E = \Gamma/2$  is equivalent to  $\delta_2$  assuming a value of  $\pi/4$  radian which is much higher than what is allowed by the Friedel sum rule. The recent *ab initio* calculation of Stocks *et al* (1972) on the variation of  $\delta_2$  with energy confirms the value  $\delta_2(E_F) \approx \pi/10$  estimated using the Friedel sum rule. The angular variation of the form

factor  $V_d''(X)$  evaluated using this value of  $\delta_2$  remains the same although its magnitude is reduced in the region  $X \approx 1$ . Curve b in figure 3 corresponds to the resistivity data computed using these form factors. In the low pressure region the agreement with the experimental curve is still good whereas a large discrepancy exists in the high pressure region. This, we believe, is due to the failure of the Ziman's resistivity formula to take into account the effects associated with multiple scattering under conditions of scattering resonances. In the low pressure region, caesium behaves as an alkali metal whereas at higher pressures it closely resembles a liquid transition metal. The recent work of Mott (1972) emphasises the non-validity of Ziman's resistivity formula for the case of liquid transition metals and his general conclusions are applicable to the present problem as well.

### 6.3. Saturation above 45 kbar

This is essentially due to the process of electron collapse being nearly complete. The variation in the resistivity with pressure in this region is due to the structure factor and form factor variations of the collapsed species.

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