J. Phys. F: Metal Phys., Vol. 2, November 1972. Printed in Great Britan.

LETTER TO THE EDITOR

Pressure induced superconductivity in cesium

G M STOCKS†‡, G D GASPARI§‖¶ and B L GYORFFY§

†Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, USA
§H H Wills Physics Laboratory, University of Bristol, Bristol, UK

MS received 5 September 1972

Abstract. Pressure induced variations in the electron–phonon coupling constant λ of cesium are calculated from first principles. We find that λ increases with pressure and predict that cesium should be superconducting with an observable transition temperature T_c at 35 kbar.

In the past five years a number of normal metals as well as some semiconductors were made to become superconductors by subjecting them to pressure (Matthias 1971, Brandt and Ginzberg 1971). An interesting example is cesium which was observed to go superconducting at the transition temperature $T_c = 1{\cdot}5$ K at a pressure of 121 kbar (Wittig 1970). The purpose of this letter is to show that, at least in Cs, the pressure induced superconductivity can be explained from essentially first principles if one assumes, as is conventional (Bardeen *et al* 1957), that the pairing force is due to electron–phonon interactions.

McMillan's solution (McMillan 1968) of the strong coupling gap equation (Eliashberg 1960, 1961, Nambu 1960, Gor'kov 1958) gives

$$T_c = \frac{\theta_D}{1{\cdot}45} \exp\left[-\left\{\frac{1{\cdot}04(\lambda+1)}{\lambda-\mu^*(1+0{\cdot}62\lambda)}\right\}\right] \tag{1}$$

where θ_D is the Debye temperature, λ is the electron–phonon coupling constant and μ^* is the electron–electron interaction parameter. For simple metals by using pseudopotential theory (Ziman 1962) and for transition metals by using the theory developed by Gaspari and Gyorffy (1972) T_c can be calculated from this formula with reasonable accuracy (Allen and Cohen 1969, Evans *et al* 1972). In this letter we shall describe a calculation of T_c using equation (1) for cesium under pressure.

When Cs is subjected to pressure its electronic structure changes drastically. As has been stressed by Stocks and Young (1969), at normal pressures the Cs crystal potential has a 'd resonance' above the Fermi energy ϵ_F in the unoccupied part of the band. We shall describe a detailed calculation which indicates that the 'resonance' is broadened but strong d scattering remains and that ϵ_F moves into this 'resonance' as the pressure increases.

‡Present address: H H Wills Physics Laboratory, Tyndall Avenue, Bristol, UK.
‖Present address: Department of Physics, University of California, Santa Cruz, California, USA.
¶Alfred P Sloan Foundation Fellow.

We evaluate the electron–phonon enhancement λ by using the relation

$$\lambda = \frac{1}{M\langle\omega^2\rangle} n(\epsilon_F)\langle I^2\rangle \tag{2}$$

where M is the atomic mass, $\langle\omega^2\rangle$ is the phonon frequency squared averaged according to the prescription given by McMillan (1968), $n(\epsilon_F)$ is the spin density of states at ϵ_F and $\langle I^2\rangle$ is the electron–phonon matrix element averaged over the Fermi surface. As was pointed out by Gaspari and Gyorffy (1972), strong d scattering near the Fermi energy plays a dominant role in determining the electronic contribution to λ, that is, $n(\epsilon_F)\langle I^2\rangle$. Therefore we shall calculate $n(\epsilon_F)\langle I^2\rangle$ rather carefully using the results of a band structure calculation but we shall be forced to use some rather crude relations to estimate $\langle\omega^2\rangle$. Nevertheless, we shall be able to conclude that, as a result of ϵ_F having moved into the 'resonance' at 35 kbar λ is considerably enhanced compared to its value at normal pressure. We then predict an observable T_c at this pressure using equation (1).

There have been a number of recent investigations of the changes in the energy band structure of Cs induced by compression (Yamashita and Asano 1970, Kmetko 1971, Averill 1971), all yielding the same general picture. In this work we have chosen to use the selfconsistent muffin tin potentials of Averill (1971) calculated using the X_α method. While it is possible to argue about the details of these potentials, that is, the neglect of

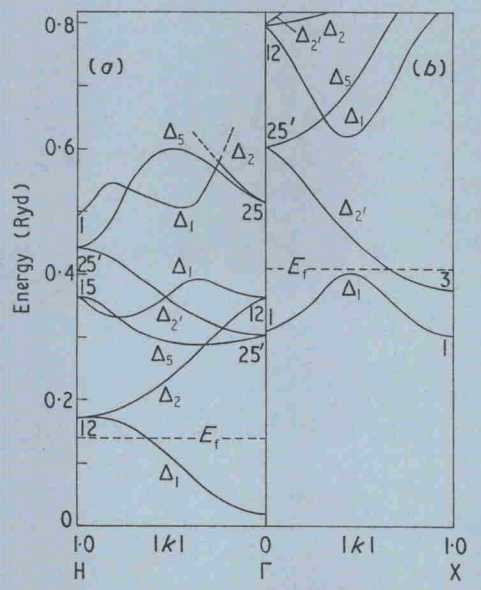

Figure 1. Energy bands in one symmetry direction for (*a*) bcc Cs at normal pressure, a=11·45 au and (*b*) fcc Cs at 35 kbar, a=10·5 au.

relativistic effects, the effect of non muffin tin corrections to the potentials at high compression, the particular choice of exchange potential, it seems likely that these potentials give the essence of the changes in the band structure which result from decreasing the volume to normal volume ratio (Ω/Ω_0).

Energy bands and phase shifts for two of Averill's (1971) potentials are shown in figures 1 and 2, these being for bcc Cs having a lattice parameter of 11·45 au ($\Omega/\Omega_0 = 1$)

and for fcc Cs having a lattice parameter of 10·5 au ($\Omega/\Omega_0 = 0{\cdot}39$). The Fermi energy is marked ϵ_F and the zero of energy is the top of the muffin tin. The calculations of the energy bands were performed by the KKR method (Korringa 1947, Kohn and Rostocker 1954), the results being identical to those of Averill, the Fermi energy was located by the methods described by Faulkner *et al* (1967).

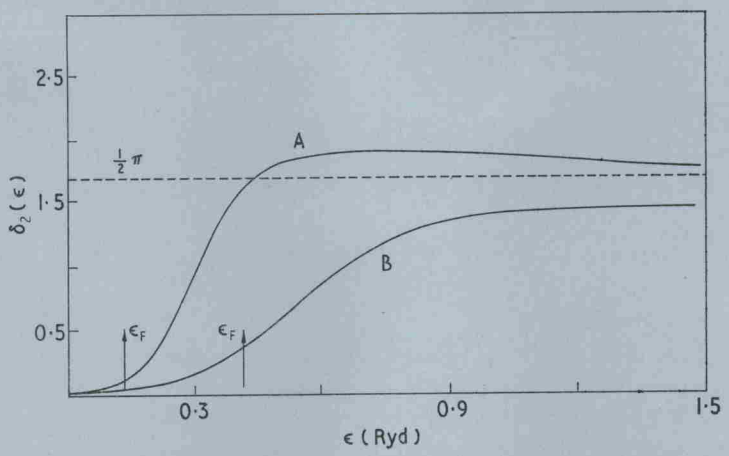

Figure 2. The d wave phase shift for bcc Cs at normal pressure (A) and fcc Cs at 35 kbar (B).

Clearly the occupied region of the energy band structure of normal volume Cs is rather free electron like (the phase shifts are small, although even here some account of the nearby d resonance is necessary). However, the unfilled region of the band structure is more characteristic of a transition metal, there being a set of d bands centred around an energy of some 0·3 Ryd above the Fermi energy. These d bands result from the rather narrow d resonance which is evident in the plot of the phase shifts. On compressing to a volume ratio of 0·39 the 'd scattering resonance' moves to higher energy and is greatly broadened resulting in a broadening of the d band. However, this is coupled with an overall lifting in energy of the conduction bands. The net result of these coupled movements is a large increase in the d character of states at the Fermi energy. Indeed, at this volume ratio, it would be fair to call Cs a monovalent transition metal. The Fermi energy phase shifts are all quite large, in particular, the phase shift difference $\delta_1 - \delta_2$ is of the order of $\frac{1}{3}\pi$, that is, it is close to a p–d resonance and it is this fact which we suggest is ultimately responsible for the occurrence of pressure induced superconductivity in this system.

It is usual in metallic systems for the bottom of the conduction band to be approximately coincidental with the top of the muffin tin potential as is the case for the normal volume calculation shown in figure 1. That this is not so for the energy bands of the compressed metal is a result of the promotion and broadening of the occupied p band immediately below the conduction band as the interatomic spacing is decreased on compression. At normal volume, this p band lies 0·63 Ryd below the muffin tinzero ϵ_0 and has negligible width, but at $\Omega/\Omega_0 = 0{\cdot}39$ it lies only 0·40 Ryd below ϵ_0 and has a width of 0·1 Ryd. The detachment of the bottom of the conduction from the muffin tin zero by some 0·3 Ryd is then a reflection of the concommitant increase in energy of the underlying core bands which results from increased overlap of core levels on neighbouring sites as the interatomic spacing is decreased.

We now use the procedure of Gaspari and Gyorffy (1972) to calculate $n(\epsilon_F)\langle I^2\rangle$ both at normal pressure ($\Omega/\Omega_0 = 1{\cdot}00$) and at 35 kbar ($\Omega/\Omega_0 = 0{\cdot}39$, see Averill 1971). This theory makes use of the rigid ion and the one electron approximations in addition to assuming a particularly simple form for the $\boldsymbol{k}$ dependence of a Bloch state. For a crystal potential of the usual spherically symmetric muffin tin form, it gives

$$n(\epsilon_F)\langle I^2\rangle = \frac{2m\epsilon_F}{(\hbar\pi)^2}\left\{2\sin^2(\delta_1-\delta_0)\frac{1}{n(\epsilon_F)} + \frac{(4\sin^2(\delta_2-\delta_1)+6\sin^2\delta_2)}{n_2^{(1)}}\frac{n_2(\epsilon_F)}{n(\epsilon_F)}\right\} \tag{3}$$

where m is the electron mass, $\hbar$ is the Planck constant, δ_0, δ_1, δ_2 are the phase shifts at ϵ_F. $n(\epsilon_F)$ is the density of spin states at ϵ_F, $n_2(\epsilon_F)$ is its $l = 2$ angular momentum component, $n_2^{(1)} = n_2(\epsilon_F)$ for a single scatterer. If $R_2(r, \epsilon)$ is the $l = 2$ scattering solution of the radial Schrödinger's equation as defined by Gaspari and Gyorffy (1972), then

$$n_2^{(1)}(\epsilon_F) = \frac{5\epsilon_F^{1/2}}{\pi}\int_0^{R_s} \mathrm{d}r\, r^2 R_2^2(r, \epsilon_F)$$

R_s being the Wigner–Seitz radius.

From the point of view of applying equation (3) to Cs under pressure, the most important qualitative feature of equation (3) is its dependence on $\delta_2(\epsilon_F)$. As ϵ_F moves closer to 'resonance' $\delta_2(\epsilon_F)$ increases rapidly and the second term inside the square bracket quickly becomes dominant. Hence, in view of our previous discussion, we may expect that for Cs at 35 kbar equation (3) will give an $n(\epsilon_F)\langle I^2\rangle$ which is greatly enhanced compared to its value at normal pressure. Thus, qualitatively, our explanation of the occurrence of superconductivity in Cs under pressure is that as the metal is compressed, ϵ_F moves up into the 'resonance', causing, through equation (3), $n(\epsilon_F)\langle I^2\rangle$ to increase. If $\langle\omega^2\rangle$ does not increase as rapidly as $n(\epsilon_F)\langle I^2\rangle$, this means that the electron–phonon coupling, that is, λ will suffer a net increase inducing a rise in T_c to the point where it is observable. This was essentially the picture envisioned by Wittig (1970), and Gandel'man and Fedorov (1971) albeit not quite in such specific terms. In what follows we shall show quantitatively that this indeed is what happens.

In order to evaluate equation (3), we must now estimate n_2†. A way of doing this is to assume that the s–p contribution to $n(\epsilon_F)$ is free electron like starting from the bottom of the s band Γ_1. By writing the free electronden sity of states function in the form (Evans *et al* 1972)

$$n^0(\epsilon_F) = \frac{1}{\pi\epsilon_F}\sum_l (2l+1)\int_0^{\sqrt{\epsilon_F}R_s} \mathrm{d}x\, x^2 j_l(x) \tag{4}$$

we estimate $n_2(\epsilon_F)$ by $n(\epsilon_F) - n_0^0(\epsilon'_F) - n_1^0(\epsilon'_F)$, where ϵ'_F is the distance of ϵ_F from ϵ_{Γ_1}. This gives us $n_2(\epsilon_F)/n(\epsilon_F) = 0{\cdot}415$ at normal pressure and 0·835 at 35 kbar. Using the results of the above band structure calculation we can then calculate $n(\epsilon_F)\langle I^2\rangle$ from equation (3). The result is that $n(\epsilon_F)\langle I^2\rangle$ increases from 0·03 eV Å^{-2} to 1·07 eV Å^{-2} as the pressure increases from zero to 35 kbar. As expected, $n(\epsilon_F)\langle I^2\rangle$ is enhanced by more than an order of magnitude due to the fact that ϵ_F moved closer to the d resonance. Unfortunately there are no neutron scattering measurements of the phonon dispersion curves in Cs at this pressure. Therefore, we approximate $\langle\omega^2\rangle^{1/2}$ by the Debye temperature θ_D, which we estimate from Lindemans law (see for example Cartz 1955) using the measured melting temperature T_m for fcc Cs at 35 kbar (Jayarman *et al* 1967, see also Wittig 1970). This gives us $\theta_D = 87$ K which leads to $\lambda = 0{\cdot}595$ at 35 kbar. This

† For a more complete discussion of ways to estimate n_2, see Evans *et al* (1972).

is a typical transition metal like value (Evans *et al* 1972) and leads to $T_c = 1{\cdot}12$ K from equation (1) using $\mu^* = 0{\cdot}13$. At zero pressure, a similar analysis cannot be carried out as $\lambda < \mu^*$ even if we take $\mu^* = 0{\cdot}11$, a value characteristic of simple metals.

To have a quantitative theory of superconductivity in Cs at 121 kbar, one should of course carry out the above analysis at that pressure. Unfortunately, this is not yet possible since there is not a selfconsistent crystal potential at 121 kbar. Moreover, it would be difficult to obtain one since beyond 42 kbar our knowledge of the crystal structure becomes rather uncertain. Nevertheless, the above calculation may be taken as a qualitative explanation. It clearly indicates that equation (3) and equation (1) can lead naturally to a rise in T_c as the pressure increases. This suggests that what is needed to explore pressure induced superconductivity is not a new mechanism for pairing but a detailed knowledge of the changes in band structure under pressure and a proper theory of electron–phonon interaction. Since in our theory the enhancement of λ is a consequence of ϵ_F having moved closer to a d resonance in the unoccupied part of the band which greatly enhances $n(\epsilon_F)\langle I^2\rangle$, one might speculate that K and Rb should also go superconducting under pressure; however, $\langle\omega^2\rangle$ also increases under pressure and whether K or Rb goes superconducting depends on whether $n(\epsilon_F)\langle I^2\rangle$ increases faster that $\langle\omega^2\rangle$. An analogous argument leads one to conjecture that the rapid variations of T_c with pressure in La (Maple *et al* 1969) is also due to rapid shifting of the d and f resonances with respect to the Fermi energy.

The prediction that $T_c = 1{\cdot}12$ K at 35 kbar can, of course, be checked experimentally. It is not inconsistent with the finding of Wittig since his experiments were not performed at temperatures below 1·3 K. Unfortunately, it is difficult to estimate the accuracy of our prediction. Experience with equation (3) indicates that it underestimates $n(\epsilon_F)\langle I^2\rangle$,

Table 1. The various parameters which are required for our calculation of $n(\epsilon_F)\langle I^2\rangle$ for both normal Cs and Cs having a volume ratio of 0·39, the latter corresponding to a pressure of approximately 35 kbar (Averill 1971)

Structure	Ω/Ω_0	R_S (au)	ϵ_F (Ryd)	$n(\epsilon_F)$ (states/Ryd atom)	δ_0	δ_1	δ_2	δ_3	δ_2^1 (Ryd^{-1})
bcc	1·00	5·638	0·1397	11·24	−0·4110	−0·1528	0·0976	0·0017	2·024
fcc	0·39	4·103	0·4138	14·13	−1·2968	−0·6873	0·3594	0·0136	2·302

on the average, by a factor of 1·5 (Evans *et al* 1972). This implies that we would have to be in error by much over 50% in our estimate of $\langle\omega^2\rangle$ if T_c is to be less than 1·12 K by an order of magnitude. Consequently, we believe that Cs will go superconducting under a pressure corresponding to $\Omega/\Omega_0 = 0{\cdot}39$ in the temperature range 1 K–0·1 K. According to Averill's calculation, this pressure is 35 kbar. However, one must bear in mind that such calculations have their own limitations and the actual pressure for $\Omega/\Omega_0 = 0{\cdot}39$ might be somewhat different.

An experimental observation of such a transition would, of course, lend strong support to the ideas expressed in this letter. In particular, it would indicate that the role assigned to the resonance in our method of calculating λ is quantitatively correct.

It would also be useful if λ was investigated, by using the present method, at other pressure points. Averill has constructed selfconsistent crystal potentials at some 10 pressures between zero and 42 kbar. It would be interesting to see in detail how λ, and

therefore T_c, changes with pressure. In this connection we note that the large shift of the d resonance with respect to ϵ_F came about because of the large change in volume, that is to say, the lattice constant. It went from 11·4 au at zero pressure to 10·5 au at 35 kbar. As is clear from the p against v diagram of Cs (Stocks and Young 1969), most of this change occurs up to 23 kbar, consequently, one would expect little change in λ after that. This suggests that one may reasonably begin to look for superconductivity right after the sudden change in volume which occurs at 23 kbar.

Finally, we would like to note that at normal pressure, we obtain $\lambda = 0{\cdot}072$. This is some 50% lower than the results of previous calculations (Schneider *et al* 1969, Animalu and Heine 1965). Unfortunately, comparison of these with our present work is rather difficult. They used pseudopotential theory and therefore they had a more consistent picture of $\langle\omega^2\rangle$. However, their calculation did not include the effect of the d resonance. Though it is fairly high above ϵ_F at normal pressure in our calculation of $n(\epsilon_F)\langle I^2\rangle$, the contribution from terms involving $\delta_2(\epsilon_F)$ was still about half of the total.

We would like to thank Dr Averill for kindly providing us with the crystal potentials for Cs under pressure. Research sponsored in part by US Atomic Energy Commission under contract with Union Carbide Corporation. One of us (BLG) would like to thank the Oak Ridge National Laboratory for the hospitality during the period of preparing this manuscript.

References

Allen P B and Cohen M L 1969 *Phys. Rev.* **187** 525–38
Animalu A O E and Heine V 1965 *Phil. Mag.* **12** 1249–70
Averill F W 1971 *Phys. Rev.* B **4** 3315–7
Bardeen J, Cooper L N and Schrieffer J R 1957 *Phys. Rev.* **106** 126–4
—— 1957 *Phys. Rev.* **108** 1175–204
Brandt N B and Ginzberg N I 1971 *Sci. Am.* **224** 83–94
Cartz L 1955 *Proc. Phys. Soc.* **68B** 951–67
Eliashberg G M 1960 *Sov. Phys.–JETP* **11** 696–702
—— 1961 *Sov. Phys.–JETP* **12** 1000–2
Evans R, Gaspari G D, Gyorffy B L 1972 *J. Phys.* F: *Metal Phys.* to be published
Faulkner J S, Davis H L and Joy H W 1967 *Phys. Rev.* **161** 556–64
Gandel'man G M and Fedorov M A 1971 *Zh. ETF. Pis. Red.* **13** 180–2
Gaspari G D and Gyorffy B L 1972 *Phys. Rev. Lett.* **28** 801–5
Gorkov L P 1958 *Sov. Phys.–JETP* **7** 505–8
Jayarman R C and McDonough J M 1967 *Phys. Rev.* **159** 527–33
Kmetko E A 1971 *Electronic Density of States* Special Publication no 323 ed L H Bennett (Washington: National Bureau of Standards) pp 67–73
Korringa J 1947 *Physica* **13** 392–400
Kohn W and Rostocker N 1954 *Phys. Rev.* **94** 1111–20
Maple M R, Wittig J and Kim K S 1969 *Phys. Rev. Lett.* **23** 1375–7
Matthias B T 1971 *Physics Today* August 23–7
McMillan W L 1968 *Phys. Rev.* **167** 331–44
Nambu Y 1960 *Phys. Rev.* **117** 648–63
Schneider T, Stoff E and Bühner W 1969 *Helv. Phys. Acta* **42** 46–50
Stocks G M and Young W H 1969 *J. Phys.* C: *Solid St. Phys.* **2** 680–93
Wittig J 1970 *Phys. Rev. Lett.* **24** 812–5
Yamashita J and Asano S 1970 *J. Phys. Soc. Japan* **29** 264–72
Ziman J M 1962 *Phys. Rev. Lett.* **8** 272–4