

Table I. Dependence of pressure (in  $10^6$  atm) on the density at  $T = 0$ 

Fe, $\rho_0=7.8$ g/cm <sup>3</sup>			Al, $\rho_0=2.7$ g/cm <sup>3</sup>			K, $\rho_0=0.862$ g/cm <sup>3</sup>			Solid Cl, $\rho_0=1.65$ g/cm <sup>3</sup>		
$\delta$	$p$	$p_{stat}$	$\delta$	$p$	$p_{stat}$	$\delta$	$p$	$p_{stat}$	$\delta$	$p$	$p_{stat}$
0.746	-0.072	0.35	1.04	0.551	0.40	0.75	-0.001		0.75	-0.010	
1.073	0.958	1.00	1.480	1.660	0.30	1.00	0.006		1.00	0.021	
2.005	7.434	9.20	1.961	3.510	1.10	2.00	0.087		2.00	0.565	-0.070
3.00	24.130	28.50	2.950	7.240	4.50	3.00	0.200	-0.155	3.00	2.130	0.325
4.00	41.00	60.50	3.500	11.08	7.40	4.00	0.193				
5.00	77.42	115.8	4.180	17.95	12.30	5.00	0.134	0.067			
6.00	127.50	175.60	5.500	35.60	25.70	6.50	0.400				
8.00	279.00	339.00	7.000	60.35	46.00	8.50	0.960				
						10.00	1.750	3.00			
						20.00	22.53	23.10			

and 4.18. We see clearly that at  $\delta = 2.95$  the  $3d_0$  band has reversed direction and goes upward. This greatly influences the level density near the Fermi surface and the electronic specific heat of aluminum.

Figures 2a-d show the energy bands in K for  $\delta$  equal to 1, 3, 5, and 10. In the normal state (Fig. 2a,  $\rho_0 = 0.862$  g/cm<sup>3</sup>) of solid K, the outer electron is at the 4s band. At a compression corresponding to  $\delta = 3$ , the important overlap of the 4s and 3d bands already takes place and exerts a great influence on the external properties of the electrons; it will be considered in greater detail in Sec. 4.

Subsequently, at  $\delta = 5$ , the 4s band is very little filled, and at  $\delta = 10$  only the 3d band is filled. This lowering of the d bands and the rising of the s bands upon compression is very characteristic of many metals, and takes place in particular in iron.

The same effect, the approach of the 3d band, but now to the 3p band, is observed in solid Cl. (It must be borne in mind that normal molecular Cl<sub>2</sub> is not described by our theory.) At  $\rho = 1.9$  g/cm<sup>3</sup> and  $k = 0$ , the 3p band has an energy  $-0.115$  at.un. and the 3d band an energy  $+0.084$  at.un. At  $\rho = 3.8$  g/cm<sup>3</sup> and  $k = 0$ , the energy of the 3p band is  $0.044$  at.un. and that of the 3d band  $0.015$  at.un. At  $\rho = 5.7$  g/cm<sup>3</sup> and  $k = 0$ , however, the 3p band is  $0.127$  at.un. above the 3d band.

## 2. DEPENDENCE OF THE PRESSURE ON THE DENSITY AT $T = 0$

It was shown in I that the pressure consists of two parts: kinetic, containing an integral over the unit-cell surface, and Coulomb, of the exchange-correlation type, which contains the interaction between electrons in different cells. The latter part of the pressure,  $p_{exch}$ , is very difficult to calculate and is evaluated for the time being by the free-electron-gas formula:

$$p_{exch} = \frac{1}{3\pi^3} \frac{e^2}{a_0^4} W^2 = 3.15 W^2 \cdot 10^6 \text{ atm},$$

where  $W$  is the difference between the Fermi energy  $E_F$  and the potential at the boundary of the cell (in atomic units).

Calculation of the kinetic pressure shows that the method of successive approximation improves the results noticeably. For example, in Fe at  $\delta = 2$ ,  $p_{kin} = 15.1 \times 10^6$  atm in first approximation, and the final value is  $p_{kin} = 10.4 \times 10^6$  atm; at  $\delta = 3$ , we have  $p_{kin} = 27.5 \times 10^6$  atm in first approximation and  $21.1 \times 10^6$  atm ultimately. In the case of aluminum the first approximation calculations are closer to the final calculations than for iron.

Table I presents the results of the calculation of the pressure at different compressions for Fe, Al, K, and solid Cl, as well as a comparison with the data of the statistical theory with quantum corrections.<sup>[3]</sup> We see that the results differ markedly. In aluminum the statistical theory gives too low a pressure, but in iron, to the contrary, the pressure is too high.

However, at large  $\delta \sim 10-12$ , for all metals there is naturally agreement between our results and the data of the statistical theory.<sup>[3]</sup> This was verified on Fe and Al.

Figure 3 shows a comparison of the calculated pressure with the data of the statistical theory for Fe. Starting with  $\delta > 2.5$ , our calculated data are in fair agreement with the experimental ones<sup>[6]</sup> in almost all metals.

In the low density region ( $\delta \sim 1$ ), the foregoing method gives both positive and negative pressure, and makes it possible to determine the calculated density of the substance at  $p = 0$ . Oscillations of the normal density  $\rho_0$  with variation of  $Z$  are also obtained. For example, the calculated normal density of K is found to be  $0.68$  g/cm<sup>3</sup>, as against the  $3.95$  g/cm<sup>3</sup> obtained from the data of the statistical