

## QUANTUM MECHANICAL THEORY OF THE EQUATION OF STATE FOR POTASSIUM, ALUMINUM, AND IRON

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The change in the nature of the electron bands of K, Al and Fe upon variation of density is considered. Results of calculation of the cold pressure are analyzed in detail and are compared with the data of the statistical theory in which quantum corrections are taken into account. The values of the electron specific heat and of the Gruneisen coefficient  $\gamma_e$  are calculated for K, Al and Fe. A considerable rearrangement of the electron bands in Al due to compression is predicted, which should lead to the appearance of negative  $\gamma_e$ . Energy overlap of the 4s and 3d bands, due to compression and resulting in a first-order phase transition in the region of negative  $\gamma_e$ , is observed in potassium.

### INTRODUCTION

WE have presented earlier<sup>[1]</sup> the results of a quantum-mechanical investigation of the equation of state of Fe (reference<sup>[1]</sup> will henceforth be cited as I). It turned out that allowance for the concrete filling of different bands in metals makes it possible to calculate more accurately the  $p(\rho)$  curve than the statistical theory with quantum correction.<sup>[2,3]</sup> We were able at the same time to explain the anomalously large electronic specific heat of Fe, something impossible in the framework of the statistical theory. Further calculations have made it possible to predict the transformation of metallic Ni compressed by a factor 6.5 into a dielectric<sup>[4]</sup> and the transformation of solid argon<sup>[5]</sup> compressed by a factor of 3 into a metal. The theory developed in I has now been noticeably improved and makes it possible to calculate with sufficient assurance the cold-pressure curve  $p(\rho)$  for many metals at a relative compression  $\delta > 2$ . This yields interesting data on the structure of the electronic energy bands at different  $\delta$ , shedding light on many properties of metals at high pressures and temperatures.

The purpose of the present work was to explain in detail recent results on Al, Fe, K, and solid Cl. In Sec. 2 we consider the change in the structure of the energy bands following change in density, in Sec. 3 we present results of calculations for the pressure, and in Sec. 4 we analyze in detail the electron specific heat and Gruneisen coefficient in a wide range of temperatures  $T$  and densities  $\rho$ .

The procedure described in I was improved in order to find solutions of the Hartree equation for

single-electron wave functions in a crystal in the Wigner-Seitz approximation. The influence of the exchange on the wave functions and the potential were not taken into account here. Subsequently exchange was taken into account approximately in the calculation of pressure.

To solve the Hartree equation, it is very important to use a successive-approximation procedure in which the first approximation is the Thomas-Fermi potential of the compressed atom. From the obtained first-approximation wave functions one finds the effective potential and the wave functions of the electron for the second approximation, etc. until the succeeding potential and wave functions do not differ from the preceding ones. We developed a procedure for improving the convergence of the successive approximation, making it possible to get along with four or five successive approximations.

### 1. ELECTRON BAND STRUCTURE AND ITS DENSITY DEPENDENCE

All the results on the dependence of the energy  $E$  on the quasimomentum  $k$  will be presented for the final solution of the Hartree equation. It must be noted that even in the first approximation the character of the bands  $E(k)$  is qualitatively the same as in the final solution. This quantitative difference, however, greatly influences the absolute value of the pressure.

Henceforth the relative compression  $\delta = \rho/\rho_0$  will always be given relative to the normal experimental density of the substance.

We start the description of the band structure