

write here only the principal components of the internal energy, which depend on the charge density distribution. According to [3], the electrostatic and kinetic energies of the valence electrons can be written in the form

$$E_c = \int_{\Omega} 2\pi \left(R_0^2 - \frac{r^2}{3} \right) \rho^2 d\Omega, \quad E_k = 2.87 e^{1/2} a_0 \rho^{3/2} \Omega,$$

and the Coulomb interaction energy of a point ionic charge with the valence electrons is

$$W_c = \int_{\Omega} \frac{ze}{r} \rho d\Omega.$$

Here the integration runs over the elementary sphere volume Ω , e is the electron charge, z is the valence, a_0 is the Bohr radius, and

$$\rho = \begin{cases} \rho_1 & \text{for } 0 \leq r \leq R_0 - \Theta, \\ \rho_1 + \delta\rho & \text{for } R_0 - \Theta \leq r \leq R_0. \end{cases}$$

Integrating and considering that

$$\rho_0 \Omega = \rho_1 \Omega_1 + (\rho_1 + \delta\rho) \Delta\Omega,$$

where ρ_0 is the density of the electron gas with a uniform distribution, $\Omega_1 = \frac{4}{3}\pi(R_0 - \Theta)^3$, $\Delta\Omega = \frac{4}{3}\pi[R_0^3 - (R_0 - \Theta)^3]$, $\rho_0 = ze/(4/3)\pi R_0^3$, we find that to order $\delta\rho^2$ the change ΔU in the internal energy of the electron gas in going from a nonuniform electron density distribution to a uniform one is

$$\Delta U = \frac{8}{15} \pi^2 \rho_1 \delta\rho R_0^5 \left[5 \left(\frac{R_0 - \Theta}{R_0} \right)^2 - 6 \left(\frac{R_0 - \Theta}{R_0} \right)^3 + \left(\frac{R_0 - \Theta}{R_0} \right)^5 \right]. \quad (2)$$

In other words, $\Delta U \geq 0$ (the roots of the equation in the square brackets are $\Theta = 0$ and $\Theta = R_0$, which corresponds to the equilibrium distribution), i.e., the transition to the more uniform spatial distribution of the electron gas density is accompanied by an increase in the role of the attractive forces. We will transform expression (2) to a form more convenient for investigation. We introduce $\delta q = \delta\rho \Delta\Omega = \text{const}$, and ρ_0 is replaced by $3ze/4\pi R_0^3$. Then

$$\Delta U = \frac{3ze}{10R_0} \delta q \left(1 - \frac{\Theta}{R_0} \right)^2 \frac{3 + 3\frac{\Theta}{R_0} - \frac{\Theta^2}{R_0^2}}{3 - 3\frac{\Theta}{R_0} + \frac{\Theta^2}{R_0^2}}. \quad (3)$$

If $\Theta/R_0 \ll 1$, we have $\Delta U \approx (3/10) \cdot (1/R_0) ze \delta q$, i.e., in the region of very low temperatures the

energy of the metal does not depend on the distribution of the valence electrons. If we retain the terms linear in Θ , then

$$\Delta U \approx \frac{3ze\delta q}{10R_0} \left(1 - 2\frac{\Theta}{R_0} \right) \frac{1 + \frac{\Theta}{R_0}}{1 - \frac{\Theta}{R_0}}. \quad (4)$$

Turning to the calculation of the temperature coefficient of the compressibility in a solid metal, we have from (1)

$$\frac{1}{\beta} \frac{d\beta}{dT} = \kappa_0 - \beta V \frac{\partial^2}{\partial V^2} \frac{\partial U}{\partial \Theta} \frac{\partial \Theta}{\partial T}. \quad (5)$$

Here κ_0 is the temperature coefficient of the compressibility with a uniform distribution of the electron density. Consequently, for sufficiently low temperatures, $(1/\beta)(d\beta/dT) \approx \kappa_0$. With increasing temperature the temperature coefficient of the compressibility increases and $(1/\beta)(d\beta/dT) > \kappa_0$ since $\partial U/\partial \Theta < 0$. In the high-temperature region, for large Θ , $\partial U/\partial \Theta$ increases perceptibly, which is accompanied by a still greater growth of $(1/\beta)(d\beta/dT)$. Such a qualitative picture is observed experimentally (see [1, 6]); at low temperatures the compressibility increases 1.5 to 2 times slower on heating than at room temperature; near the melting point the temperature dependence of the compressibility becomes quite nonlinear.

Incidentally we note that the mechanism under consideration decreases the temperature coefficient of the bulk expansion of a solid metal in comparison to the liquid. To be specific we consider alkali metals. According to [3], for a uniform distribution of the electron density we have the following expression for the energy:

$$U = -\frac{C}{R} + \frac{B}{R^3},$$

in which the equilibrium distance R_0 between the centers of ions, which is found from the condition $\partial U/\partial R = 0$, is $(3B/C)^{1/2}$, where B and C are certain constants. In such a treatment R_0 does not depend on temperature and the bulk expansion coefficient is determined by anharmonic effects only. Taking (3) into account gives an additional dependence of R_0 on the temperature, so that for quite low temperatures the mechanism under consideration does not contribute to α , while for higher temperatures we have

$$\alpha = \alpha_0 + \frac{3}{2} \frac{1}{B} \frac{\partial U}{\partial \Theta} \frac{\partial \Theta}{\partial T} < \alpha_0,$$

where α_0 is the bulk thermal expansion coefficient for a uniform distribution of electronic charge.