

THE COMPRESSIBILITY OF METALS

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Experimental results indicate that the temperature coefficient of the compressibility of metals is larger in the solid state than in the liquid state, although the bulk expansion coefficient α in the solid metal is significantly less than in the liquid metal. It is shown that this effect can be related to the nonuniform volume distribution of the valence electron gas density in solid metals. A transformation from a nonuniform to a uniform distribution increases the temperature coefficient of the compressibility and decreases α .

Investigations of the temperature dependence of the compressibility β in metals in the solid [1] and liquid [2] state have shown that the temperature coefficient of the compressibility in the solid metal is somewhat greater than in the liquid, although according to theory [3] the increase of β with temperature is related to an increase of the interatomic distance, i.e., $(1/\beta)(d\beta/dT) \sim \alpha$ (α is the temperature coefficient of the volume expansion), while $\alpha_{\text{sol}} < \alpha_{\text{liq}}$. The indicated experimental fact is probably not fully accounted for by the change of the carrier effective mass with temperature, or by various types of structural transformation, since it is observed in all metals which have been studied, including alkali and noble metals (for example silver) in which heating is not accompanied by these features. Evidently this effect is related to the presence in all solid metals of a nonuniform distribution of charge density. In [4] it was shown how taking the screening of the valence electrons into account within the framework of perturbation theory leads to an increase of the wave function in the region R_0 ($2R_0$ is the distance between the centers of ions). In the Wigner-Seitz approximation this is equivalent to assuming that in the peripheral regions of the elementary sphere the density of the valence electron gas is $\rho_1 + \delta\rho$ (ρ_1 is the density over the remaining part of the sphere). From very general arguments one can conclude that the intensification of the thermal motion of the ions on heating leads to a more uniform distribution of the electron density. In liquid metals, due to the absence of long-range order, the density of the valence electron

gas is practically uniform immediately after melting [5].

We can show that this mechanism leads to an increase in the temperature coefficient of the compressibility in a solid metal in comparison to the liquid. Actually, if $(T/\beta)(\partial\beta/\partial T)_V \ll 1$ we have for the isothermal compressibility

$$\frac{1}{\beta} = V \left(\frac{\partial^2 U}{\partial V^2} \right)_T. \quad (1)$$

Here U is the internal energy of the metal and V is the volume.

The construction of a rigorous quantum theory of the cohesive forces in a metal encounters a whole series of difficulties; therefore, the dependence of U on V will be estimated on the basis of the statistical theory of metals [3]. Such an approach in the present case is also quite convenient because within the framework of statistical models the difference between a liquid and a solid metal vanishes, since long-range order is not assumed. In this model the internal energy is composed of the kinetic energy of the electron gas, the electron-ion attraction energy, and the ion-ion interaction energy (the appearance of the latter term is related to the overlap of the inner electron shells of neighboring ions; this always occurs in polyvalent and noble metals). We assume that the transition to a more uniform distribution of the valence electron density does not much alter the ionic interaction, and also the depth to which the conduction electrons penetrate the electronic orbitals of the ions [3]; therefore, we will

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.

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