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Abstract

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PHYSICS

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THE GRÜNEISEN CONSTANT IN THE THOMAS-FERMI APPROXIMATION

(Presented by Academician Ya. B. Zel' dovich, 2 XI 1964)

The equation of state of a solid at temperatures above the Debye temperature and up to the melting point has the well-known form

$$p(v,T) = p(v,0) + 3\gamma(v)kT/v, \tag{1}$$

$$\gamma(v) = -d\ln\omega/d\ln v. \tag{2}$$

The thermal pressure in (1), proportional to the temperature T, is due only to harmonic vibrations of the nuclei; here $\overline{\ln\omega}$ is the mean logarithm of their frequencies; $\gamma(v)$ is the so-called Grüneisen constant, depending only on the atomic volume v. The contribution from the anharmonicity of nuclear vibrations and from thermal excitation of electrons is usually small up to the melting point.

The literature contains quite complete calculations of the cold pressure $p(v,0)$, which have been carried out for spherized cells of a monatomic crystal lattice: 1) by the Thomas-Fermi method (^{1}), 2) by the Thomas-Fermi method with exchange and quantum corrections (^{2}), 3) by the Hartree method with a certain correction for exchange (^{3}). However, similar calculations for $\gamma(v)$ are lacking. In the present work a first step in this direction is made.

To calculate $\omega(k)$ it is necessary to know the interatomic forces, which reduce to electrostatic forces (see Feynman' s theorem (^{4})) arising from the redistribution of all charges under a small displacement of nuclei from lattice sites. We shall take the displacements of the nuclei to be proportional to e^{ikn}, where k is a given wave vector and n is the position vector of the site from which the nucleus is displaced. Applying the perturbation method in the Thomas-Fermi approximation, we obtain an equation for the change in the lattice potential

$V_\alpha(r,k)$ due to displacement of the nuclei in the specified manner along the axis α with unit amplitude

$$\Delta V_\alpha(r,k) = 4\pi Z \frac{\partial \delta(r)}{\partial r_\alpha} + 4\left(\frac{3}{\pi}\right)^{1/3} \rho^{1/3}(r) V_\alpha(r,k) \tag{3}$$

in the region of one crystal cell with Bloch conditions on its boundary; $\rho(r)$ is the electron density for an ideal periodic lattice. The further approximation consists in spherizing the cell.

Equation (3) was solved by expanding $V_\alpha(r,k)$ in spherical harmonics in the form developed in the work of G. M. Gandel' man (^{3}). The only difference is that to the Wigner-Bloch conditions on the sphere (of radius r_0) there is added an inhomogeneous condition at zero because of the singularity in (3). The eigenfrequencies $\omega(k)$ are the eigenvalues of the matrix

$$\Lambda_{\alpha\beta}(k) = \omega_0^2 \frac{r_0}{3} \left[\frac{\partial}{\partial r_\beta}(V_\alpha(r,k) - V_\alpha(r,0))\right]_{r=0}, \tag{4}$$

where ω_0 is the Langmuir frequency of the unscreened nuclei, i.e.

$$\omega_0^2 = 4\pi(Ze)^2/Mv. \tag{5}$$

For a spherized cell it turns out that matrix (4) is diagonal and two of its diagonal elements are equal to one another, i.e., the waves are strictly longitudinal and transverse, and there are only two elastic moduli, as for an isotropic solid. From these moduli the Poisson coefficient σ and the bulk modulus were calculated. The latter, as a check, was also calculated directly by differentiating the function $p(v,0)$; the difference lies within the computational error ($< 0.1\%$). The Grüneisen constant $\gamma(v)$ was calculated by formula (2). The results of the calculations for 6 harmonics (for 8 they practically do not differ) are presented in Table 1, where the logarithms are decimal and the atomic volume v is measured

Table 1

$-\lg Zv$	$-\lg \omega/\omega_0$	γ	σ	$-\lg Zv$	$-\lg \omega/\omega_0$	γ	σ
∞	0.277	0.500	0.500	22.728	0.742	0.797	0.350
29.154	0.282	0.503	0.497	22.294	0.886	0.868	0.335
27.676	0.291	0.510	0.492	21.684	1.142	0.974	0.317
26.202	0.318	0.529	0.476	21.211	1.386	1.055	0.307
24.993	0.374	0.570	0.446	20.798	1.630	1.122	0.300
24.227	0.444	0.619	0.417	20.061	2.128	1.226	0.291
23.770	0.508	0.660	0.397	19.405	2.630	1.300	0.287
23.323	0.590	0.712	0.376	18.630	4.134	1.366	0.283

in cubic centimeters. We note that in the Debye model of the spectrum the Debye temperature θ is related to the mean frequency by the relation

$$\overline{\ln \hbar\omega} = \ln k\theta - \frac{1}{3}. \tag{6}$$

In the limit $v \to 0$ the electrons are distributed uniformly and the screening of the nuclei by the electrons becomes inessential; therefore

$$\overline{\ln \omega} = \ln(\mathrm{const} \cdot \omega_0) \tag{7}$$

and, according to (5) and (2), $\gamma \to \frac{1}{2}$. The value of the constant in (7) can also be calculated for cubic lattices, using the necessary Coulomb sums from work (5); the constant is equal to:

0.528 for the spherized cell,

0.543 for a b.c.c. lattice,

0.547 for an f.c.c. lattice.

In addition, as $v \to 0$ the shear modulus tends to zero (6), and therefore $\sigma \to \frac{1}{2}$, as for a liquid.

At normal density most elements lie in the region $\lg Zv = 21 \div 22$, then $\gamma = 0.9 \div 1.1$; $\sigma = 0.30 \div 0.33$, $\theta = 250 \div 800$°K; the corresponding experimental quantities are: $\gamma = 1.0 \div 2.5$; $\sigma = 0.30 \div 0.37$; $\theta = 100 \div 400$°K. Better agreement cannot be expected; let us recall that in the Thomas–Fermi method the pressure $p(v, 0)$ goes to zero only at zero density.

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Note: Figure translations are in progress. See original paper for figures.