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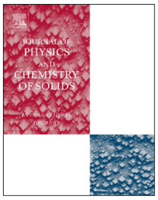

# Plasma frequency approach to estimate the Debye temperature of the ionic crystals and metal alloys

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ABSTRACT

A novel method is proposed to calculate the Debye frequency, speed of sound, and some other properties of ionic crystals and metal alloys from the plasma frequency of the ions. As an example of application, the theoretically obtained Debye temperatures $T_D$ of NaCl, KCl, RbI, AgBr, $Cu_3Au$ are 308 K, 238 K, 98 K, 149 K, and 296 K respectively, while an experiment gives 321 K, 235 K, 103 K, 140 K, and 285 K respectively. The reliability of calculated values of $T_D$ of the univalent and bivalent pure metals is characterized by $R^2 \simeq 0.985$. The hypothetical properties of solid under extremal conditions were estimated. For example, the metallic hydrogen has the theoretical determined $T_D \simeq 4000$ K and the speed of sound 20 km c$^{-1}$ at a pressure of 2.60 Mbar.

## 1. Introduction

Historically, the first quantum model of solids has been suggested by Einstein. It was declared that all the points of lattice (the atoms) of solid are the isolated oscillators with the same frequency, $\omega_E$. However, as it is well known, the low temperature dependence of Einstein specific heat is wrong. Debye has shown that this wrong theoretical result is due to the atoms considered as isolated oscillators, but the real atoms of solid are the bonded oscillators, so that their oscillations are correlating with volume of whole piece of solid. To correct the Einstein model, Debye takes into account the normal collective atom oscillation modes instead of the individual oscillations of isolated atoms. Thus, in the Debye model, all the points of lattice are oscillating with consistency in phase, amplitude and frequency.

According to the Debye model of crystalline solid, there is a maximum frequency of the elastic vibrations, $\omega_D$ (Debye cutoff frequency) [1–3]. In this approximation, the dispersion relation has a linear form $\omega = c_s k$, where $c_s$ is the constant velocity of sound, $k$ is the wavevector. The various physical properties of solids such heat capacity, speed of sound, thermal expansion, melting temperature, compressibility can be expressed in terms of the Debye frequency or Debye temperature $T_D$ [4].

The approximation of experimental specific heat dependence on the temperature with the Einstein model gives the numeric value of $\omega_E$ which is close to $\omega_D$. Analogously, the mean square of thermal atomic displacements in lattice obtained by both mentioned models has the similar values (Appendix A).

In framework of the Debye model, the methods of determining the Debye temperature can be divided into two categories: calorimetric, based on measurement of temperature dependence of the heat capacity at low temperature; and calculation of $T_D$ from the elastic constants, based on the three phase velocities for propagation of elastic waves in the crystal, averaged over all directions. In addition, there are the semi-empirical approaches, which employ the different lattice properties such as raw data (dielectric permittivity, interionic distance, etc.).

These methods use the small wavevector part of dispersion relation. Thereafter, $\omega_D$ is estimated by extrapolating to high wavevectors. However, due to a linear approximation of dispersion law, it is possible to determine $\omega_D$ based on the data on the high wavevectors those correspond to the cutoff frequency immediately. Really, the wavelength of $\omega_D$ -mode approaches the distance between the adjacent atoms. Therefore, Debye frequency can be also considered as an eigenfrequency of the atom vibration in local potential well that is determined by all surrounded atoms of the crystal.

The Debye frequency can be estimated by ab initio methods, for example, from the quantum chemistry computation of the energy of point of lattice in the crystal. However, such calculations require too much computing resources. For certain types of solids, the

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satisfactory theoretical estimation of $\omega_D$ can be obtained without resorting to quantum chemistry computations. It has been shown in [5] that the speed of sound into metal crystals can be theoretically obtained from the ionic plasma frequency [6,7].

A simplest approach to estimate the Debye frequency of metals and ionic crystals is proposed. A good estimation of the Debye temperature and the speed of sound for a wide range of pure metals and ionic crystals can be obtained from the approximation of the Debye cutoff frequency of an acoustic phonons spectrum of metal by the ionic plasma frequency. In this paper, for the first time such a method has been developed to estimate the Debye temperature and other properties of the ionic crystals such as the alkali-halides and the crystal metal alloys.

## 2. Model

The ionic binding in the ionic crystals is due to the Coulomb interaction. A high frequency oscillation of the charged ions in the ionic crystal lattice can be described by development of Langmuir–Tonks model of plasma vibration [6]. It is necessary to take into account the ions of different masses and charges in the ionic crystals.

To calculate the ions frequency, we suppose that the electric charge density of ensemble of $j$-th type ions is given by $\rho_j = \rho_{0j} + \delta\rho_j$, where $\rho_{0j} = \text{const}$ is a mean equilibrium charge density, $\delta\rho_j$ is a small density perturbation, $|\rho_{0j}| \gg |\delta\rho_j|$. Analogously, the velocity of $j$-type ions motion is $\mathbf{v}_j = \mathbf{v}_{0j} + \delta\mathbf{v}_j$, where $\mathbf{v}_{0j}$ is a mean velocity of heat motion in thermodynamic equilibrium (so that $\mathbf{v}_{0j} = 0$ ), $\delta\mathbf{v}_j$ is a perturbation of equilibrium velocity of ions.

The equation of continuity is given by

$$\dot{\rho}_j = -(\nabla \rho_j \mathbf{v}_j) \simeq -\rho_{0j}(\nabla \delta\mathbf{v}_j), \tag{1}$$

since $\delta\mathbf{v}_j \nabla \delta\rho_j$ can be neglected as an equation term of second infinitesimal order. Differentiating with respect to time, we obtain the expression

$$\delta\ddot{\rho}_j = -\rho_{0j}(\nabla \delta\dot{\mathbf{v}}_j). \tag{2}$$

The equation of ions fluid motion is given by

$$\rho_{0j}\delta\dot{\mathbf{v}}_j = \frac{q_j}{m_j}\rho_{0j}\mathbf{E}, \tag{3}$$

where $q_j$ and $m_j$ are a charge and a mass of an ion of $j$-th type respectively, $\mathbf{E}$ is an electric field strength vector. After differentiating both parts of Eq. (3) by space gradient operator $\nabla$, we obtain the expression

$$\rho_{0j}(\delta \nabla \dot{\mathbf{v}}_j) = \frac{q_j}{m_j}\rho_{0j}(\nabla \mathbf{E}). \tag{4}$$

Maxwell–Poisson equation is $(\nabla \mathbf{E}) = \varepsilon_0^{-1}\sum_k \rho_k$, where the summation is over all types of ions. Taking into account the electroneutrality of complete ensemble of all types of ions $\sum_k \rho_{0k} = 0$, we obtain

$$(\nabla \mathbf{E}) = \frac{1}{\varepsilon_0}\sum_k \delta\rho_k. \tag{5}$$

Substituting (4) into (2) with account of (5), we get the equation

$$\delta\ddot{\rho}_j = -\omega_{0j}^2 \sum_k \delta\rho_k, \tag{6}$$

where the so-called plasma frequency (or Langmuir frequency) of $j$-th type of ions is given by

$$\omega_{0j} = \sqrt{\frac{q_j^2 n_{0j}}{\varepsilon_0 m_j}}, \tag{7}$$

where $n_{0j} = \rho_{0j}/q_j$ is a mean concentration of $j$-th type of the ions.

Analogously, the vibration eigenfrequency of valence electrons in metal is defined by an expression $\omega_e = \sqrt{e^2 n_e/(\varepsilon_0 m_e)}$, where $e$, $n_e$, $m_e$ are the elementary charge, concentration of the free (valence) electrons, and electron effective mass respectively. This value, called a plasmon frequency, is an important parameter in optics of the metals [8].

Denoting in Eq. (6) the total electric charge density perturbation as

$$\delta\rho = \sum_k \delta\rho_k, \tag{8}$$

then after the summation in (6) over all $j$-th types of ions, we obtain

$$\delta\ddot{\rho} = -\omega_0^2 \delta\rho, \tag{9}$$

where the combined plasma frequency is given by expression

$$\omega_0 = \sqrt{\sum_j \omega_{0j}^2}. \tag{10}$$

Consider a simple ionic crystal as NaCl containing two types of ions with masses $m_1$ and $m_2$ (reduced mass is $m = m_1 m_2/(m_1 + m_2)$ ), and the effective electric charges $q_1 = q$ and $q_2 = -q$. In this case, Eq. (10) with account of Eq. (7) can be rewritten as

$$\omega_0 = q\sqrt{\frac{n_0}{\varepsilon_0 m}} = q\sqrt{\frac{\rho_m}{\varepsilon_0 m_1 m_2}}, \tag{11}$$

where $n_0 = \rho_{01}/q_1 = \rho_{02}/q_2$ is a mean concentration of each types of ions; $\rho_m = (m_1 + m_2)n_0$ is a mass density of the crystal.

In case of the ionic crystal as $CaCl_2$, the effective ionic charges are $q_1 = 2q$ and $q_2 = -q$. Taking into account the electroneutrality of solid, the ionic concentrations values are $n_1 = n_0$ and $n_2 = 2n_0$; $\rho_m = (m_1 + 2m_2)n_0$. Eq. (10) with account of Eq. (7) gives the expression

$$\omega_0 = q\sqrt{\frac{2n_0}{\varepsilon_0}\left(\frac{2}{m_1} + \frac{1}{m_2}\right)} = q\sqrt{\frac{2\rho_m}{\varepsilon_0 m_1 m_2}}. \tag{12}$$

Analogously, consider a binary metal alloy containing two types of ions with masses $m_1$ and $m_2$, and the positive ionic electric charges $q_1$ and $q_2$. In this case, we obtain

$$\omega_0 = \sqrt{\frac{q_1^2 n_{01}}{\varepsilon_0 m_1} + \frac{q_2^2 n_{02}}{\varepsilon_0 m_2}}, \tag{13}$$

where $\rho_m = m_1 n_{01} + m_2 n_{02}$ is a mass density of an alloy.

Particularly, in case of simple metal, we obtain

$$\omega_0 = q\sqrt{\frac{n_0}{\varepsilon_0 m}} = \frac{q}{m}\sqrt{\frac{\rho_m}{\varepsilon_0}}, \tag{14}$$

where $m$ and $q$ are the ionic mass and the effective electric charge respectively, $\rho_m \simeq m n_0$ is a mass density of a metal crystal.

Since the solid crystal is an appreciably more compact system of ions than Langmuir plasma, consequently the van der Waals interactions of ions (as London's dispersion forces [3,9]) and also the friction forces should be taken into account.

Therefore, instead of Eq. (9), we obtain

$$\delta\ddot{\rho} = -\Omega^2 \delta\rho - 2\gamma\delta\dot{\rho}, \tag{15}$$

$\Omega^2 = \omega_0^2 + \omega_W^2$, where $\omega_W^2$ is an additional elasticity of the potential well of the ion, elasticity which corresponds to the van der Waals forces contribution for the small ion oscillation amplitudes; $2\gamma$ is a friction coefficient.

If $\gamma < \Omega$, then frequency of the ions free oscillations in accordance with Eq. (15) is given by the expression

$$\omega_i = \sqrt{\Omega^2 - \gamma^2}, \tag{16}$$