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Calculation of the pressure dependence of the bulk modulus using a jellium model

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Abstract

We evaluate the electronic contribution to the pressure dependence of the bulk modulus B of pure metals using an effective jellium model to characterize the electronic density. The partial derivative $n = \partial B/\partial P$ evaluated at zero pressure (and at constant temperature) is the main parameter on which the Murnaghan equation of state depends. The general features of this method are discussed and the corresponding results are compared with experimental data.
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1. Introduction

The problem of finding an equation of state (EOS) for solids for extended P–V–T conditions is rather complicated and different authors have faced the problem from different points of view [1–3]. A useful simplification of the problem has been to study the EOS at zero temperature [4–6]. Other authors have made assumptions that arise from some regularities in the experimental data. Among these types of EOS, the work by Murnaghan [7] that leads to the so-called Murnaghan EOS (M-EOS) is particularly remarkable. This is based on the assumption of a bulk modulus (B) linear with pressure, valid for most of the systems at low pressure. In this M-EOS, the derivative of the bulk modulus to pressure ($n = \partial B/\partial P|_T$) at zero pressure is a key parameter and is taken as a constant, most of all due to the lack of reliable information about its thermal dependence. Several attempts have been made to take into account the effects on the M-EOS of a temperature dependence of n [8]. Recently, one of the authors [9] has published data on the thermal dependence of n using the "universal" EOS for the zero-temperature P–V relation and a Debye–Grüneisen approximation for modeling the thermal pressure $\partial P/\partial T|_V$. The n thermal dependence was obtained for 23 different elements along the periodic table, and the results suggest that the slope $\partial n/\partial T$ is always positive. In the present work, we face the problem from another point of view. The value of n can be directly related to the dependence of the bulk modulus on the volume. The relation between B and V at zero temperature has been recently shown by two of the authors [10] to be accurately described by considering only the electronic contribution to the bulk modulus, even when this contribution is considered through the non-stabilized jellium model (NS-jellium). Taking the mentioned relation between the bulk modulus and the volume available for one electron in the jellium, characterized here by the value of r_s the radius of a sphere of equal volume, we are able to find the electronic contribution to the value of n. The obtained values have shown to be about 30% of the n value suggesting that lattice contributions are not negligible.

2. Theoretical model for B and n

One of the most useful ways of characterising the properties of elements through the periodic table is by means

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of their electronic density ρ_0. In the jellium model all the information about the spatial configuration of the electronic density is considered negligible, i.e. ρ_0 is considered as a constant. In this case, ρ_0 can be described in terms of r_s as $\rho_0^{-1} = 4\pi r_s^3/3$. Clearly, the jellium approximation will correctly describe properties strongly dependent on the free-electron-like component of the density [11,12]. As was shown in [10] one of these properties is the bulk modulus and more generally the elastic properties of the elements that are mostly determined by the interstitial electronic density. The bulk modulus is thus mainly determined by the compression properties of the electron gas. Hence [13],

$$B = \frac{1}{12\pi r_s}\left(\frac{\partial^2\varepsilon}{\partial^2 r_s^2} - \frac{2}{r_s}\frac{\partial\varepsilon}{\partial r_s}\right), \tag{1}$$

where ε is the energy per particle in the system. Three main contributions to ε must be taken into account, the kinetic energy, the exchange energy and the correlation energy. The kinetic energy can be written as $\varepsilon_{kin} = \frac{3}{5}\alpha^2 r_s^2$ and the exchange contribution as $\varepsilon_{ex} = -\frac{3}{2}\pi\alpha r_s$ with $\alpha = (\frac{4}{9}\pi)^{1/3}$. The correlation energy ε_{corr} is always negative. At metallic densities it goes from 0.1 to $0.5\varepsilon_{ex}$ and in the limit of high densities it is proportional to $\ln r_s$ [11]. By taking the corresponding derivatives of each term according to (1) we find that [10]

$$B = \begin{cases} B_{kin} + B_{ex} + B_{corr} & \text{if } r_s \leqslant 1, \\ B_{kin} + \frac{B_{ex}+B_{corr}}{r_s} & \text{if } r_s > 1, \end{cases} \tag{2}$$

which not only includes transition metals but also alkali metals. At this point, we have a complete expression for $B(r_s)$. Let us now derive the value of n starting from its definition and assuming that at constant temperature P is a function of V. Using the bulk modulus and taking into account that $V = \frac{4}{3}\pi r_s^3 N$ (with constant N), we obtain the following analytical equation:

$$n = -\frac{1}{3}\frac{r_s}{B}\frac{\partial B}{\partial r_s}, \tag{3}$$

which is a simple and, however, powerful tool to calculate the pressure dependence of the bulk modulus of metals.

3. Results and discussion

As we showed in the previous section, we consider r_s^3 as a measure of the volume of the solid and we obtain an expression for n (Eq. (3)) that can be directly used for the elements of the periodic table. However, two main questions arise at this point. First, it is not clear that r_s is a good measure of the volume, most of all due to the assumption of a constant N during compression. Second, metals are not in equilibrium at their corresponding r_s values, but they must be kept under external pressure. Since it is not clear that a specific solid property at pressures different from zero can be correctly obtained from the zero pressure value, it will be strongly dependent on how sensitive the chosen property is on the spatial electronic density distribution.

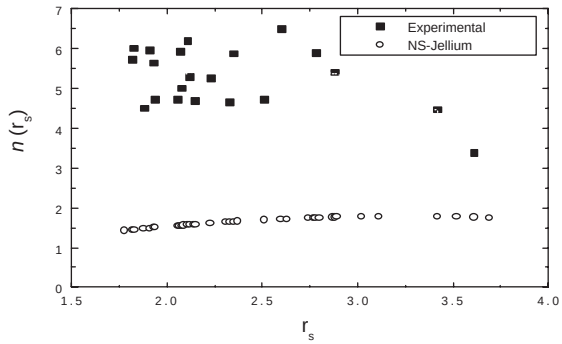

Fig. 1. Experimental values of n taken from the literature [1–10] along with the predicted electronic contribution calculated using an NS-jellium model. The agreement increases with increasing r_s.

In fact, the other important way in which the electrons can produce deviations from the jellium under pressure is the Fermi surface topology. By reducing r_s, from simple metal values to transition metal values, the Fermi surface undergoes many different changes of shape and connectivity: on varying the number of electron per atom, the density and r_s vary, and, correspondingly, the Fermi level crosses Van Hove singularities. By moving the Fermi level up and down, electron and hole pockets and necks open or disrupt, producing the so-called electronic topological transitions [14]. Correspondingly, the metal free energy can vary with sharp singularities, because work is required to open or disrupt a Fermi surface pocket or neck.

Nevertheless, we will try to answer the question of how dependent the n parameter is on electronic properties. As we saw, n is the derivative of B with respect to pressure, so it will be a measure of the "stability" of the jellium approach to the description of Bulk modulus. In the case of an s-type solid with large values of r_s we can expect the jellium approach to be a good approximation. However, it can also be expected that this approximation fails to describe properties of p- and d-type metals under pressure.

Fig. 1 shows the experimental values of n together with the corresponding values that arise from the NS-jellium model. As can be seen, values from the jellium model are always about 1.5 whereas experimental values are about 5. Values for Ca or K which have r_s values of around 3.5 have n values near 3, i.e. they are better described by the NS-jellium model than the rest of metals, as expected.

Fig. 2 shows the ratio n/n_j with n_j the electronic contribution to n calculated from the NS-jellium model. As can be seen the ratio is always about 30% and increasing for large values of r_s.

Values for the n parameter have been obtained from an NS-jellium model. The electronic contribution to n seems to be around 30%, increasing to 50% for p- and d-type solids.

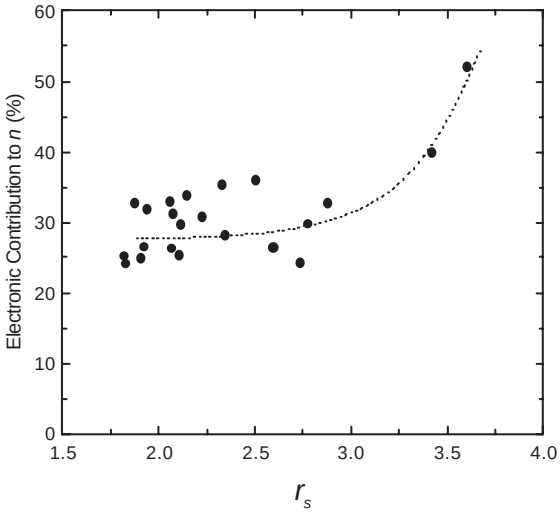

Fig. 2. Percentage of electronic contribution to n as a function of r_s. The dotted line is a guide to the eye.

As was previously mentioned, NS-jellium requires external pressure to act upon it. This external stabilization can be replaced by an equivalent internal pressure due to neglected ion-core terms in the total energy.

Acknowledgements

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