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THE COMPRESSIBILITY PROBLEM AND VIOLATION OF THE CAUCHY RELATIONS IN METALS

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The relation between static and dynamic (derived from the vibrational problem) compressibilities of a metal is analyzed. Both quantities are shown to be identical, however, provided only that the contribution of many-particle interaction between ions via the conduction electrons is taken into account. The nature of violation of the Cauchy relations in non-transition metals is investigated. Two causes of such violation are found to exist. One is related to the presence of many-particle interaction and the second to the existence of the electron fluid. The equation of state is derived and the problem of stability of simple metals is analyzed. It is shown that the stability of metals of the Na or K type depends to a great degree on the non-pointlike character of the ions or on the deviation of the electron interaction from a pure Coulomb interaction.

1. INTRODUCTION

IN modern theory of metals there are two problems that have been widely discussed in recent years but have no final solution. These are the problems of compressibility and of the violation of the Cauchy relations in metals.

The gist of the first problem, in short, can be formulated as follows. Should the dynamic compressibility, i.e., the compressibility obtained from measurements of the speed of sound, coincide in metals, where an important role is played by the electron fluid, with the static compressibility, which is defined as the second derivative of the energy with respect to the volume?

If we analyze the customarily employed expressions for the dynamic matrix and for the total energy, then it turns out that they lead to non-identical values of the compressibility. At first glance this seems natural, since the static compressibility is determined by all the terms that contribute to the total energy of the metal, whereas the dynamic compressibility is made up only of the terms that correspond to the oscillation problem. On the other hand, the dynamic problem for a metal is considered at a constant electron density, whereas in the static case there enter in explicit form terms corresponding to changes of the density, and consequently to a change of the dielectric constant. All this has raised doubts concerning the possibility of obtaining the compressibility of metals from dynamic measurements.

We show in this paper, however, that although all the foregoing problems actually exist, a consistent analysis leads to the conclusion that the static and dynamic compressibilities are exactly equal. It is very important that this result is obtained only when account is taken of the contribution made by the multi-ion interaction, which was introduced and discussed in detail in our preceding papers[1-3]. An essential factor in the solution of this problem is also the possibility of finding an exact solution for the limit of the long-wave phonons in the presence of many-particle forces[3].

The second problem is connected with a clarification of the nature of the violation of the Cauchy conditions in metals. As is well known, when the interaction between the atoms has a paired character, a definite connection exists between the elastic moduli (the Cauchy relations)[4] or the corresponding speeds of sound. This connection is clearly observed, for example, in ionic crystals. In non-transition metals, where there is practically no overlap of the ionic cores, the interaction between the ions has a direct Coulomb character or is indirect, via the conduction electrons. If the indirect interaction is represented simply as one producing a screening of the Coulomb interaction between the ions, then we arrive at a purely paired character of the forces. A more consistent analysis, based on the determination of the energy of the electron gas in second order in the electron-ion interaction, also leads, at first glance, to a paired interaction between the ions[5]. It has been experimentally established, however, that the Cauchy condition is not satisfied in all metals. One possible explanation of this fact was given in[2]. In metals, actually, a very important role may be played by many-particle interactions between the ions via the conduction electrons, imitating forces of the covalent type[1,2]. This immediately eliminates the initial premises that lead to the Cauchy relation. However, there certainly exist metals where the many-particle forces are small, and yet the Cauchy condition is not satisfied. For example, in Na and K, the experimentally measured phonon spectrum[6,7] is well described in the approximation of paired interaction forces, but the Cauchy relations are not satisfied in these metals. We present in this paper a complete analysis of this problem, whereby it is possible to trace consistently the nature of the violation of the Cauchy relations. It turns out here that this violation is due to the very existence of the electron fluid in the metal.

In addition, we analyze in this paper a number of related problems, particularly the equation of state and the cause of the stability of simple metals of the Na type. It is shown that the stability at ordinary densities is ensured only by the fact that the ion is not point-like (by the deviation of the electron-ion scattering amplitude from the purely Coulomb case as $q \to 0$).

2. COMPRESSIBILITY OF A METAL

We consider a metal with one atom per unit cell, a total number of atoms N, a number of electrons $N_e = ZN$, and a total volume Ω. Assume that the temperature is T = 0. Then the static compressibility κ is written in the following form:

$$1/\kappa = B = \Omega(\partial^2 E/\partial\Omega^2)_N. \tag{2.1}$$

(We have introduced here the reciprocal compressibility B or the modulus of compression.)

The expression for the total energy of the metal, contained in (2.1), is represented in the form

$$E = E_i + E_e. \tag{2.2}$$

Here E_i is the energy of the ion lattice and E_e is the energy of the electrons in the field of the fixed ions, which, according to[1,3], can be represented in the form of a series in powers of the pseudopotential (we shall henceforth assume the pseudopotential to be local):

$$E_e = E^{(0)} + E^{(1)} + E^{(2)} + \ldots \tag{2.3}$$

We neglect the energy of the zero-point oscillations and consider a purely static energy, corresponding to a regular arrangement of the ions in the metal. We then have for E_i

$$\begin{aligned} E_i &= \frac{1}{2} \sum_{n\neq n'} \sum_{\mathbf{q}\neq 0} \frac{4\pi Z^2 e^2}{\mathbf{q}^2\Omega} \exp\{i\mathbf{q}(\mathbf{R}_n - \mathbf{R}_{n'})\} \\ &= \frac{1}{2} N \sum_{\mathbf{K}\neq 0} \frac{4\pi Z^2 e^2}{\mathbf{K}^2\Omega_0} - \frac{1}{2} \sum_{\mathbf{q}\neq 0} \frac{4\pi Z^2 e^2}{\mathbf{q}^2\Omega_0} \end{aligned} \tag{2.4}$$

(Ω_0 is the volume per unit cell). We have taken into account here the electric neutrality of the system, which leads to a cancelation of all the Coulomb parts at q = 0. As the result, there is no K = 0 term in (2.4).

The first term of the series (2.3) is the energy of the interacting electron gas. The corresponding compression modulus, defined in accordance with (2.1), will be denoted by $B^{(0)}$.

The next terms of the series (2.3) for the regular static lattice can be written in the form[1,3]

$$E^{(n)} = \Omega \sum_{\mathbf{K}_1 \ldots \mathbf{K}_n} \Gamma^{(n)}(\mathbf{K}_1 \ldots \mathbf{K}_n) V_{\mathbf{K}_1} \ldots V_{\mathbf{K}_n} \Delta(\mathbf{K}_1 + \ldots + \mathbf{K}_n). \tag{2.5}$$

(we shall henceforth use the notation of[3].) In the term with n = 1, the momentum conservation law yields $\mathbf{K} = 0$. The value of $\Gamma^{(1)}(0)$ was determined in[3]:

$$\Gamma^{(1)}(0) = n_0$$

(n_0 is the electron density).

When account is taken of the electric neutrality in the initial Hamiltonian of the electron-ion system for the pseudopotential V_q at q = 0, only the non-Coulomb part of the interaction remains

$$V_{\mathbf{q}=0} = b/\Omega_0, \tag{2.6}$$

although at small values of $\mathbf{q}$ the limiting expression is of the form

$$V_{\mathbf{q}\to 0} = -\frac{4\pi Z e^2}{\mathbf{q}^2\Omega_0} + \frac{b}{\Omega_0}. \tag{2.7}$$

(We note that in (2.5) all the $\mathbf{K}_i \neq 0$, for when $\mathbf{K}_i = 0$ the contribution from (2.6) vanishes as the result of the presence of the multipoles $\Gamma^{(n)}(\mathbf{K}_1, \ldots, \mathbf{K}_n)$ of the dielectric constant $\epsilon(\mathbf{K}_i = 0)$ in the denominator[1,3].) As the result we have

$$E^{(1)} = NbZ/\Omega_0, \tag{2.8}$$

and accordingly we get for the compressibility

$$B^{(1)} = 2bZ/\Omega_0^2. \tag{2.9}$$

the energy $E^{(2)}$ can be readily found by taking it into account that (see[1])

$$\Gamma^{(2)}(\mathbf{q}, -\mathbf{q}) = -\frac{1}{2}\frac{\Pi(\mathbf{q})}{\varepsilon(\mathbf{q})}, \quad \varepsilon(\mathbf{q}) = 1 + \frac{4\pi e^2}{\mathbf{q}^2}\Pi(\mathbf{q}). \tag{2.10}$$

As noted by us earlier[1,3], and as can also be readily seen directly from (2.5), each succeeding term of the expansion of the energy introduces an additional factor (V_K/ϵ_F), which is the small parameter of the problem.

We shall confine ourselves henceforth in the analysis of the static compressibility to results that are obtained with accuracy to $V_K/\epsilon_F)^2$ inclusive. This corresponds to retaining $E^{(2)}$ in the energy and neglecting terms $E^{(n)}$ with $n \geq 3$. In this approximation, the total energy is written in the form

$$E = E_i + E^{(0)} + \frac{ZNb}{\Omega_0} - \frac{\Omega}{2} \sum_{\mathbf{K}\neq 0} |V_{\mathbf{K}}|^2 \frac{\Pi(\mathbf{K})}{\varepsilon(\mathbf{K})}. \tag{2.11}$$

In determining the compressibility corresponding to (2.11), it is necessary to take into account the fact that the energy $E^{(2)}$ depends on the volume in three ways. First, explicitly; second, via the dependence of the reciprocal-lattice vectors $\mathbf{K}$ on the dimensions of the direct lattice Ω_0, and third, via the dependence of the polarization operator $\Pi(\mathbf{q})$ (and consequently also the dielectric constant) on the electron-gas density n_0. Therefore the derivative with respect to the volume in (2.1) can be represented in the following form (the differentiation is at constant N throughout):

$$\frac{\partial}{\partial\Omega} = \left(\frac{\partial}{\partial\Omega}\right)_{\mathbf{K}, n_0} - \frac{1}{3\Omega} K_\alpha \left(\frac{\partial}{\partial K_\alpha}\right)_{\Omega, n_0} - \frac{n_0}{\Omega}\left(\frac{\partial}{\partial n_0}\right)_{\Omega, \mathbf{K}}. \tag{2.12}$$

The form of the second term in (2.12) presupposes a similar variation of the unit cell of the direct (and by the same token of the reciprocal) lattice with variation of the volume. In a cubic crystal, when we are interested in the variation of the volume of the crystal following a change in the external pressure, this assumption is automatically satisfied. We confine ourselves henceforth to the case of cubic symmetry. The appearance of the last term in (2.12) is a direct consequence of the specific nature of the metal. There is no such term in crystals of another type.

Taking the foregoing into consideration, we obtain after direct differentiation of (2.10)

$$\begin{aligned} B = B^{(0)} + \frac{2bz}{\Omega_0^2} + \frac{1}{\Omega_0} \sum_{\mathbf{K}\neq 0} \left[\varphi(\mathbf{K}) + \frac{5}{9} K_\alpha \frac{\partial\varphi(K)}{\partial K_\alpha} + \frac{1}{18} K_\alpha K_\beta \frac{\partial^2\varphi(K)}{\partial K_\alpha \partial K_\beta}\right] \\ - \sum_{\mathbf{K}\neq 0} \left\{\frac{1}{2} n_0^2 |V_{\mathbf{K}}|^2 \frac{\partial^2}{\partial n_0^2}\left(\frac{\Pi(\mathbf{K})}{\varepsilon(\mathbf{K})}\right) + 2n_0 |V_{\mathbf{K}}|^2 \frac{\partial}{\partial n_0}\left(\frac{\Pi(\mathbf{K})}{\varepsilon(\mathbf{K})}\right)\right. \\ \left. + \frac{1}{3} n_0 K_\alpha \frac{\partial}{\partial K_\alpha}\left[|V_{\mathbf{K}}|^2 \frac{\partial}{\partial n_0}\left(\frac{\Pi(\mathbf{K})}{\varepsilon(\mathbf{K})}\right)\right]\right\}, \end{aligned} \tag{2.13}$$

where

$$\varphi(\mathbf{q}) = \frac{4\pi Z^2 e^2}{\mathbf{q}^2\Omega_0} - |V_{\mathbf{q}}|^2 \frac{\Pi(\mathbf{q})}{\varepsilon(\mathbf{q})}\Omega_0. \tag{2.14}$$

The third term in (2.13) is the result of allowance for E_i and differentiation of $E^{(2)}$ with respect to the volume at a fixed electron density, i.e., of retaining only the first two terms in (2.12). We took into consideration the fact that at fixed N the second term of (2.4) does not depend on the volume at all, and in addition, by definition, $V_q \sim 1/\Omega_0$. The last term in (2.13) is the result of allowance for the change of the electron density with volume and is connected with the third term in (2.12).

We now turn to consider the dynamic compressibility. It is defined for cubic crystals in the following manner:

$$1/\varkappa = B = {}^1/_3(C_{11} + 2C_{12}). \qquad (2.15)$$

The expressions for the elastic moduli C_{11} and C_{12}, with account taken of the many-particle interaction, accurate to terms of order $(V_K/\epsilon_F)^2$ inclusive, were obtained in[3] from the solution of the dynamic problem. We take into consideration formulas (2.20) and (4.4) of the cited paper, and use the identity (see[3])

$$B^{(0)} = n_0^2/\Pi(0). \qquad (2.16)$$

Then, after direct transformations, we obtain for the dynamic compressibility (2.15) an expression that coincides exactly with the static compressibility (2.13).

This result is far from trivial, for it is necessary to take into account the terms $E^{(0)}$, $E^{(1)}$, and $E^{(2)}$ of the expansion (2.3) in the static approach, as against the terms $E^{(2)}$, $E^{(3)}$, and $E^{(4)}$ in the dynamic approach (see[3]). We shall therefore discuss it in somewhat greater detail. The term $E^{(2)}$ in the energy expansion (2.3) depends, as can be readily seen, on the coordinates of the ion pairs. At a fixed volume, it is simply the effective paired interaction between the ions. However, when the volume changes, a change takes place not only in the distance between the ions (at a fixed character of the interaction) but also in the interaction itself, as the result of the change of the electron density. Thus, the interaction between the ions in the metal acquires a unique unpaired character, although this character is obtained also in the static problem from the term $E^{(2)}$. This unpaired character leads to the compressibility contribution described by the last term of (2.13). It is interesting that the equivalent contribution in the dynamic problem arises already from the clearly unpaired interaction corresponding to allowance for the three-particle and four-particle indirect interactions between the ions via the conduction electrons[3]. We emphasize therefore that since in all the investigations proceeding[1] no account was taken in the dynamic matrix at all of the multiparticle interaction, and all the results are equivalent to inclusion of $E^{(2)}$ only, no equality of the static and dynamic compressibilities could be obtained at all.

The third term in (2.13), which is not connected with the differentiation with respect to the density, corresponds already to the usual pair interaction and is obtained in the dynamic problem from the contribution made to the matrix $D_1^{\alpha\beta}(q) + D_2^{\alpha\beta}(q)$ from the umklapp processes $(\mathbf{K} \neq 0)$[3].

Finally, the compressibility $B^{(0)}$ of the electron gas (and also the term $B^{(1)}$ (2.9)) results in the dynamic problem from the term with $\mathbf{K} = 0$ in $D_1^{\alpha\beta}(q) + D_2^{\alpha\beta}(q)$ in the limit as $q \to 0$ (see[3]).

In this connection, it must be emphasized that the equality of the corresponding contributions to the compressibility is attained only as the result of the existence of a relation between the compressibility of the electron gas and the polarization operator at q = 0 (2.16), a relation that is valid in the exact theory of the electron gas. At the same time, this relation, generally speaking, does not hold in the approximate theory (for example, it is strongly violated in the random-phase approximation[8]). This was one more reason why the dynamic compressibility did not coincide with the static one when the concrete calculations were compared. We emphasize, in particular, that to obtain correct results for the phonon spectrum of metals it is necessary to use for the polarization operator an approximate expression satisfying the relation (2.16) (see[2,3]).

It should also be noted that nowhere in the preceding arguments did we use the equilibrium condition. Therefore, the proof of the equality of the dynamic and static compressibilities remains valid also for a metal subjected to homogeneous deformation (under pressure).

3. NATURE OF VIOLATION OF THE CAUCHY RELATIONS IN METALS

As is well known (see, for example,[4]), if it is assumed that the interaction between atoms in a crystal has a paired character, then the elastic moduli, must satisfy definite relations, the so-called Cauchy relations

$$C_{\alpha\beta,\gamma\delta} = C_{\alpha\gamma,\beta\delta}.$$

For cubic crystals, there exists a single Cauchy relation

$$C_{12} = C_{44}. \qquad (3.1)$$

In ionic crystals, the Cauchy relations are well satisfied[4]. The question why the Cauchy relations are not satisfied in metals has so far remained open. The point is that, as is customarily assumed, the forces in simple cubic metals have a predominately paired character. This is confirmed, for example, by measurements of the background spectrum in alkali metals[6,7], when the dispersion curves obtained experimentally could be described with the aid of paired forces only. It might therefore seem that the Cauchy relations should be satisfied in metals, but they are not satisfied in any metal, even in the simplest one.

Let us analyze this problem by using the developed notions concerning the electron-ion system of a metal[1,3]. We use the expressions obtained in[3] for the elastic moduli. After simple transformations, taking into account the fact that the function $\varphi(\mathbf{K})$ (2.14) depends only on the modulus $|\mathbf{K}|$, and also the cubic symmetry of the crystal, we obtain

$$\begin{aligned} C_{12} - C_{44} = {} & \frac{n_0^2}{\Pi(0)} + \frac{2bn_0}{\Omega_0} + \frac{1}{\Omega_0}\sum_{\mathbf{K}\neq 0}' \left\{\varphi(\mathbf{K}) + \frac{1}{3}K_\alpha \frac{\partial\varphi(\mathbf{K})}{\partial K_\alpha}\right\} \\ & - \sum_{\mathbf{K}\neq 0}' \left\{2n_0|V_{\mathbf{K}}|^2 \frac{\partial}{\partial n_0}\left(\frac{\Pi(\mathbf{K})}{\varepsilon(\mathbf{K})}\right) + \frac{1}{3}K_\alpha \frac{\partial}{\partial K_\alpha}\left[|V_{\mathbf{K}}|^2 \frac{\partial}{\partial n_0}\left(\frac{\Pi(\mathbf{K})}{\varepsilon(\mathbf{K})}\right]\right) \right. \\ & \left. + \frac{1}{2} n_0^2 \frac{\partial^2}{\partial n_0^2}\left(\frac{\Pi(\mathbf{K})}{\varepsilon(\mathbf{K})}\right)\right\}. \end{aligned} \qquad (3.2)$$

The Cauchy relation, as is well known (see[4]), presupposes a crystal equilibrium corresponding to a pressure P = 0. Therefore, using the results of the preceding section, let us find a general expression for the pressure. In accordance with (2.2) and (2.3), we have

$$P = P_i + P^{(0)} + P^{(1)} + P^{(2)} + \sum_{n\geqslant 3} P^{(n)}. \qquad (3.3)$$

The pressure $P^{(0)}$ of the interacting electron gas, by definition, is given by

$$P^{(0)} = -\partial E^{(0)} / \partial \Omega. \tag{3.4}$$

It can be obtained also by integrating the expression for the reciprocal compressibility of the electron gas (2.16). Integrating by parts, we get

$$P^{(0)} = \frac{1}{2}\frac{n_0^2}{\Pi(0)} - \frac{1}{2}\int_0^{n_0} dn_0 n_0^2 \frac{\partial}{\partial n_0}\left(\frac{1}{\Pi(0)}\right). \tag{3.5}$$

Further, $P^{(1)}$ is determined by the contribution made to the energy from the non-Coulomb part of the electron-ion interaction as $q \rightarrow 0$ (see (2.8)):

$$P^{(1)} = bZ / \Omega_0^2. \tag{3.6}$$

The contribution from the terms $E_i + E^{(2)}$ to the energy is determined in analogy with the procedure employed in the preceding section for the compressibility:

$$P_i + P^{(2)} = \frac{1}{2\Omega_0}\sum_{\mathbf{K}\neq 0}\left\{\varphi(\mathbf{K}) + \frac{1}{3}K_\alpha\frac{\partial\varphi(\mathbf{K})}{\partial K_\alpha}\right\} - \frac{1}{2}n_0\sum_{\mathbf{K}\neq 0}|V_\mathbf{K}|^2\frac{\partial}{\partial n_0} \times\left(\frac{\Pi(\mathbf{K})}{\varepsilon(\mathbf{K})}\right). \tag{3.7}$$

The last term in (3.3) is the contribution made to the pressure by the multi-ion interaction. We confine ourselves here to a consideration of the pressure with accuracy up to $(V_\mathbf{K}/\epsilon_F)^2$ inclusive, i.e., with the same accuracy with which (3.2) was derived.

Therefore the general expression for the pressure (it actually is the equation of state of the metal) is written in the following form:

$$P = \frac{1}{2}\frac{n_0^2}{\Pi(0)} + \frac{bn_0}{\Omega_0} + \frac{1}{2\Omega_0}\sum_{\mathbf{K}\neq 0}\left\{\varphi(\mathbf{K}) + \frac{1}{3}K_\alpha\frac{\partial\varphi(\mathbf{K})}{\partial K_\alpha}\right\} - \frac{1}{2}\int_0^{n_0} dn_0 n_0^2\frac{\partial}{\partial n_0}\left(\frac{1}{\Pi(0)}\right) - \frac{1}{2}n_0\sum_{\mathbf{K}\neq 0}|V_\mathbf{K}|^2\frac{\partial}{\partial n_0}\left(\frac{\Pi(\mathbf{K})}{\varepsilon(\mathbf{K})}\right). \tag{3.8}$$

It is easy to see that if we neglect now in (3.8) and (3.2) the terms in which there is a derivative with respect to the electron density, then the equilibrium condition $P = 0$ immediately leads to $C_{12} - C_{44} = 0$, i.e., to the satisfaction of the Cauchy relation.

However, as follows from the preceding section, the presence of derivatives with respect to the density is a direct manifestation of the unpaired character, typical of metals, of the interaction between ions. We therefore should retain these terms. Then, taking into account the equilibrium condition $P = 0$ and transforming (3.2) accordingly, we obtain the following final expression, which demonstrates in explicit form the violation of the Cauchy relation:

$$C_{12} - C_{44} = \int_0^{n_0} dn_0 n_0^2\frac{\partial}{\partial n_0}\left(\frac{1}{\Pi(0)}\right) - \sum_{\mathbf{K}\neq 0}\left\{n_0|V_\mathbf{K}|^2\frac{\partial}{\partial n_0}\left(\frac{\Pi(\mathbf{K})}{\varepsilon(\mathbf{K})}\right) + \frac{1}{3}K_\alpha\frac{\partial}{\partial K_\alpha}\left[|V_\mathbf{K}|^2\frac{\partial}{\partial n_0}\left(\frac{\Pi(\mathbf{K})}{\varepsilon(\mathbf{K})}\right)\right] + \frac{n_0^2}{2}\frac{\partial^2}{\partial n_0^2}\left(\frac{\Pi(\mathbf{K})}{\varepsilon(\mathbf{K})}\right)\right\}. \tag{3.9}$$

In order to analyze this result in more traditional language, let us transform the general expression (2.11) for the energy, separating explicitly in it the interaction between the pairs of ions $\varphi(\mathbf{R}_n - \mathbf{R}_{n'})$. Adding the term with $q = 0$ to the sum and performing the inverse transformation in direct space, we obtain

$$E = E^{(0)} - \frac{N}{2}\frac{n_0 Z}{\Pi(0)} + \frac{\Omega}{2}\sum_\mathbf{q}|V_\mathbf{q}|^2\Gamma^{(2)}(\mathbf{q}, -\mathbf{q}) + \frac{1}{2}\sum_{n\neq m}\varphi(\mathbf{R}_n - \mathbf{R}_m),$$

where

$$\varphi(\mathbf{R}) = \frac{1}{N}\sum_\mathbf{q}\varphi(\mathbf{q})e^{i\mathbf{q}\mathbf{R}}, \tag{3.10}$$

and $\varphi(q)$ is defined in accordance with (2.14).

At a fixed volume, the last term in (3.10) is the usual expression for the crystal energy at a paired character of the interaction between the atoms. If we retain in the energy expansion only $E^{(2)}$, then the phonon spectrum of the metal will be determined just by this term.

Solving the dynamic problem in this approximation and determining accordingly the elastic moduli (see[3]), we get

$$C_{12} - C_{44} = -\frac{1}{3\Omega}\sum_{n\neq m}\left(\frac{\partial\varphi(R)}{\partial R}R\right)_{R=|\mathbf{R}_n-\mathbf{R}_m|}. \tag{3.11}$$

On the other hand, if we assume that the equilibrium of the metal is due only to paired forces, then the pressure is determined by differentiating only the last term in (3.10) with respect to the volume (at fixed density). Then

$$P = -\frac{1}{6\Omega}\sum_{n\neq m}\left(\frac{\partial\varphi(R)}{\partial R}R\right)_{R=|\mathbf{R}_n-\mathbf{R}_m|}. \tag{3.12}$$

As the result we have obtained the usual expressions for the paired interaction, and the equilibrium condition $P = 0$ leads directly to the Cauchy relation.

Starting from these expressions and comparing them with (3.2) and (3.8), we can easily establish the existence of general causes of violation of the Cauchy relation. The first is that the paired forces themselves do not cause equilibrium of the metal. It is necessary to take into account in explicit form the existence of an electron fluid. Formally this corresponds to the need for taking into account the change of the electron density with change of volume when the transition is made from (3.10) to (3.12). This leads to the appearance in the right side of (3.12) of an additional term equivalent to the fourth term in (3.8). (It is easy to show that the first three terms in (3.8) coincide exactly with (3.12).) It is interesting that in this case an important contribution is made by the first terms in (3.10), the role of which is not manifest in the dynamic problem, where the equilibrium condition $P = 0$ is not used at all.

The second cause of the violation is the unpaired character of the indirect interaction between the ions. In the dynamic problem this has led to the need for taking into account in the calculation with accuracy to $(V_\mathbf{K}/\epsilon_F)^2$, of the contributions from $E^{(3)}$ and $E^{(4)}$, which led to the appearance of the last term in (3.2), and by the same token to violation of the simple relation (3.11), which is equivalent to the first three terms of (3.2). On the other hand, as we have already noted, the very dependence of $\varphi(R)$ on the density, which is revealed upon differentiation with respect to the volume, causes, generally speaking, the same unpaired character of the interaction between ions. This, in turn, leads to one more contribution to the pressure, described by the last term in (3.8).

The two noted causes taken jointly lead to violation of the Cauchy relation, which is described in explicit form by the final expression (3.9).

It is interesting that the contribution due to the first cause can be expressed simply in terms of the pressure and the compressibility of the electron gas. Indeed, using (3.5), we have

$$(C_{12}-C_{44})_1=\int_0^{n_0} dn_0 n_0^2\frac{\partial}{\partial n_0}\left(\frac{1}{\Pi(0)}\right)=-2P^{(0)}+\frac{1}{\varkappa^{(0)}}. \quad (3.13)$$

The simplicity of this expression makes it possible to estimate easily the contribution of (3.13) to the total difference (3.9) for concrete metals. To this end, we can use, for example, the Nozieres-Pines interpolation formula for the energy of the electron gas[8]. For Na and K respectively we then get (in units of 10^{11} dyne/cm^2) $(C_{12}-C_{44})_1 = 0.176$ and $(C_{12}-C_{44})_1 = 0.096$. The experimental values of the elastic moduli give for these differences the values 0.092 and 0.059 for Na and K, respectively. It is interesting that even for these simple metals the structural terms in (3.9) are very significant and make a contribution to (3.9) of the same order as (3.13).

Within the framework of the consistent description of Na and K, as given in[9], in which all terms of (3.9) are taken into account, we have obtained the values $(C_{12}-C_{44})_{\mathrm{Na}} = 0.078$ and $(C_{12}-C_{44})_{\mathrm{K}} = 0.060$, which are in good agreement with experiment.

4. EQUATION OF STATE. STABILITY OF SIMPLE METALS

The expression obtained in the preceding section for the pressure (3.8) is actually the equation of state of the metal at T = 0

$$P=\Phi(\Omega_0), \quad (4.1)$$

obtained accurate to $(V_K/\epsilon_F)^2$ inclusive. Under normal conditions $P \approx 0$, and consequently

$$\Phi(\Omega_0)=0. \quad (4.2)$$

This equation, for a known pseudopotential, makes it possible in principle to obtain the equilibrium volume of the unit cell. Actually, however, the pseudopotential is known with much lower accuracy than the volume of the unit cell. Therefore in practice Eq. (4.2) should be regarded as an independent condition superimposed on the pseudopotential, which makes it possible, in particular, to determine one parameter when the pseudopotential is parametrically specified (see[2]).

In metals such as Na and K, the Fourier components of the pseudopotential at the reciprocal-lattice points are relatively small (see, for example,[2]). This makes it possible to neglect the term $E^{(2)}$ in a semiquantitative analysis (the "zero-order model"). Then the equation of state can be approximately written in the form

$$P=P^{(0)}+\frac{bZ}{\Omega_0^2}-\frac{1}{3}\alpha\frac{Z^2e^2}{\Omega_0^{4/3}}. \quad (4.3)$$

The last term is the expression for P_i, which can be determined from the energy of the ion lattice of the cubic crystal

$$E_i=-\frac{1}{2}\alpha\frac{Z^2e^2}{\Omega_0^{1/3}}. \quad (4.4)$$

(The quantity α is connected with the Madelung constant and is equal to $\alpha = 1.792(4\pi/3)^{1/3}$ for a body-centered lattice.) Accordingly we obtained for the compressibility in the zero-order model

$$\frac{1}{\varkappa}=\frac{Z^2}{\Omega_0^2\Pi(0)}+\frac{2bZ}{\Omega_0^2}-\frac{4}{9}\alpha\frac{Z^2e^2}{\Omega_0^{4/3}}. \quad (4.5)$$

From the form of expressions (4.3) and (4.5) and from a direct estimate of the terms contained in them we arrive at the interesting conclusion that the non-Coulomb part of the electron-ion interaction, i.e., the terms with b, play a very important role in the stability of simple metals. If we assume the model of point-like ions, for which b = 0, then the pressure and the compressibility turn out to be negative, and the metal is unstable in a wide range of values of the density or Ω_0 near the true equilibrium value.

In order to verify this more rigorously, we use the results of a complete calculation performed for Na and K in[9], where, naturally, all the terms for the equation of state and the compressibility were taken into account. These results are listed in the table. We note that we have used here the same notation as in (3.3), and the same type of expansion was used for B.

The foregoing data confirm that the stability of simple metals is connected to a decisive degree with the deviation of the scattering amplitude as $q \to 0$ from the value corresponding to the pure Coulomb case (see (2.7)), i.e., with the inaccuracy or the internal structure of the ion.

This explains why hydrogen, in which b = 0 automatically, is not stable in the metallic phase at normal densities and differs greatly in its properties from the series of elements of the first group. We note that when the density is considerably increased, owing to the growth of ϵ_F, an important role is assumed by $P^{(0)}$ and $B^{(0)}$, and this can lead to stability of the metallic phase for the model of point-like ions and hence, in principle, for hydrogen. This corresponds to high densities ($r_s \sim 1.6$). We note that the problem of metallic hydrogen was investigated by Abrikosov[10].

From the results given in the table we see also how far from reality, even for simple metals, the "jelly" model, in which only the contribution from $P^{(0)}$ and $B^{(0)}$ is taken into account. In fact, there exist much larger contributions, resulting from the discrete arrangement of the ions (P_i and B_i) and from the fact that they are not point-like ($P^{(1)}$, $B^{(1)}$). We note that these two contributions are entirely different in nature and their competition is decisive for the determination of the equilibrium value of Ω_0.

In connection with the importance of the terms with b in the foregoing analysis, it is meaningful to discuss here the more general definition of this quantity, corresponding to non-local electron-ion interaction. In this case, the Hamiltonian for the electron system in the field of the fixed ions takes in the second-quantization representation the form[1,2]

$$\begin{aligned}H=&\sum_{\mathbf{K}}\frac{K^2}{2m}a_{\mathbf{K}}^{+}a_{\mathbf{K}}+\frac{1}{2}\sum_{\mathbf{K},\mathbf{K}',\mathbf{q}}\frac{4\pi e^2}{\mathbf{q}^2}a_{\mathbf{K}-\mathbf{q}}^{+}a_{\mathbf{K}'+\mathbf{q}}^{+}a_{\mathbf{K}'}a_{\mathbf{K}}\\&+\sum_{\mathbf{K}}U_{\mathbf{K},\mathbf{K}}a_{\mathbf{K}}^{+}a_{\mathbf{K}}+\sum_{\mathbf{K},\mathbf{q}\neq 0}U_{\mathbf{K},\mathbf{q}+\mathbf{K}}a_{\mathbf{K}}^{+}a_{\mathbf{K}+\mathbf{q}},\end{aligned} \quad (4.6)$$

where

$$U_{\mathbf{K},\mathbf{K}+\mathbf{q}}=\frac{1}{N}\sum_m e^{i\mathbf{q}\mathbf{R}_m}V_{\mathbf{K},\mathbf{K}+\mathbf{q}}.$$

(In (2.5), $V_{K,K+q}$ has been replaced by the value corresponding to the local interaction V_q.) The last term in

	Values in 10^{11} dyne/cm^2			Values in 10^{11} dyne/cm^2	
	Na	K		Na	K
$P^{(0)}$	0,042	—0.033	$B^{(0)}$	0.260	0,029
$P^{(1)}$	0.929	0,444	$B^{(1)}$	1.858	0.888
$P^{(2)}$	—0.093	—0,039	$B^{(2)}$	—0,204	—0,053
P_i	—0,878	—0,372	B_i	—1.171	—0,495
P	0	0	B	0.743	0,369

(4.6) gives the contribution made to the expansion of the energy in powers of the pseudopotential (2.3), starting with $E^{(2)}$. The value of $E^{(1)}$ is determined entirely by the third term in (4.6) and equals

$$E^{(1)} = \sum_{\mathbf{K}} V_{\mathbf{K},\mathbf{K}} n_{\mathbf{K}}, \tag{4.7}$$

where $n_{\mathbf{K}}$ are the occupation numbers. (There is no Coulomb part in $V_{\mathbf{K},\mathbf{K}}$.) In the case of local interaction we have

$$V_{\mathbf{K},\mathbf{K}} = b/\Omega_0$$

(see (2.6)) and, taking into account the exact condition

$$\sum_{\mathbf{K}} n_{\mathbf{K}} = NZ,$$

we arrive at (2.8). Retaining precisely this form for $E^{(1)}$, we obtain in the general case

$$b = \frac{\Omega_0}{NZ} \sum_{\mathbf{K}} V_{\mathbf{K}\mathbf{K}} n_{\mathbf{K}}. \tag{4.8}$$

Formula (4.8) makes it possible to obtain the value of b if the pseudopotential is specified in nonlocal form, for example for a model potential introduced by Heine and Abarenkov (see, for example,[5]). The last circumstance is very important, since it makes it possible to use a pseudopotential determined from independent experimental data (from spectroscopic data in the Heine-Abarenkov case).

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[1] E. G. Brovman and Yu. Kagan, Zh. Eksp. Teor. Fiz. 52, 357 (1967) [Sov. Phys.-JETP 25, 232 (1967)].

[2] Yu. Kagan and E. G. Brovman, Neutron Inelastic Scattering (Proc. Symp. Copenhagen), 1 IAEA, Vienna, (1968), p. 3.

[3] E. G. Brovman and Yu. Kagan, Zh. Eksp. Teor. Fiz. 57, 1329 (1969) [Sov. Phys.-JETP 30, 699 (1970)].

[4] M. Born and K. Huang, Dynamical Theory of Crystal Lattices, Oxford, 1955.

[5] H. Harrison, Pseudopotentials in the Theory of Metals, Benjamin, N. Y., 1966.

[6] A. D. B. Woods, B. N. Brockhouse, R. H. March, A. T. Stewart, and R. Bowers, Phys. Rev. 128, 1112 (1962).

[7] R. A. Cowley, A. D. B. Woods, and G. Dolling, Phys. Rev. 150, 487 (1966).

[8] D. Pines and P. Nozieres, Theory of Quantum Liquids, Benjamin, N. Y., 1966.

[9] E. G. Brovman, Yu. Kagan, and A. Kholas, Preprint IAE-1887; Fiz. Tverd. Tela [Sov. Phys.-Solid State], in press.

[10] A. A. Abrikosov, Zh. Eksp. Teor. Fiz. 39, 1797 (1960); 41, 551 (1961); 45, 2038 (1963) [Sov. Phys.-JETP 12, 1254 (1961)]; 14, 395 (1962)]; 18, 1399 (1965)].

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