

AN ANALYSIS OF THE STATIC AND DYNAMIC PROPERTIES OF METALS AND IN PARTICULAR OF MAGNESIUM (THE ROLE OF MANY-ION INTERACTION)

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Submitted November 5, 1970

Zh. Eksp. Teor. Fiz. 61, 737–752 (August, 1971)

The theoretical scheme previously developed for describing a many-electron and many-ion system is applied for the first time to the analysis of a large number of properties of diatomic metals, particularly magnesium. The only unknown quantity required for the calculations, viz., the electron-ion interaction pseudopotential, is determined from the long-wave characteristics (two equilibrium conditions, shear modulus, and optical frequency for $q = 0$). The remaining quantities can then be found without free parameters and can be employed to verify the theory. These quantities, viz., the four remaining elastic moduli, binding energy, phonon spectrum throughout the whole phase volume, and the equation of state, are very close to those found experimentally (with an accuracy to within 1–5%). The equation of state of a non-monatomic crystal is found theoretically for the first time. The role of terms of third order in the pseudopotential is analyzed in all cases and found to be considerable. The results obtained show that a large number of metal properties may be described quantitatively.

1. INTRODUCTION

WE have developed in earlier papers^[1-3] a many-particle theory of metals a characteristic feature of which was consistent description of the effective interaction between the ions via the conduction electrons, leading in particular to allowance for interionic forces of the unpaired type. The physical quantities, such as the energy of the metal, the pressure, the elastic moduli, etc., are presented in the form of a series in powers of the effective electron-ion interaction (pseudopotential), which actually reduces to expansion in powers of the small parameter V_K/ϵ_F (V_K is the Fourier component of the pseudopotential for a momentum equal to the reciprocal-lattice vector K). The electron-electron interaction is taken into account in each term of this series and enters the theory in the form of universal multipoles that depend only on the density of the electron fluid and do not depend on the concrete properties of the metal.

The developed theoretical scheme is free, to a considerable degree, of the principal difficulties encountered by both the traditional band theory of metals (see, for example,^[4]) and the modern theory of metals, which uses the pseudopotential method (see, for example,^[5]).

In the band scheme, the difficulty lies in the need for correct allowance for the interaction between the electrons, as obtained in the single-electron approximation. The corresponding wave functions ("Bloch functions") vary concretely from metal to metal, and their use for the calculation of the interaction energy entails great difficulties. As a rule, the Bloch functions are replaced by plane waves in this case in the calculations, but the accuracy of this approximation cannot be estimated in practice, much less improved. At the same time, this interaction makes an appreciable contribution to the structure-dependent part of the energy, which is of precisely of greatest interest.

In the standard pseudo-potential approach, the structure-dependent part of the energy is written in the form of the paired interaction energy of the ions^[6] or

"neutral pseudoatoms"^[6]. This approximation, which has maximum simplicity, was used for the analysis of the binding energy, the elastic moduli, and phonons (see, for example,^[5-11]) in the simplest metals. The confinement to only paired forces of interion interaction, however, made it possible in most cases to claim only qualitative agreement with experiment. The only exceptions are alkali metals, in which the unpaired interaction is anomalously weak (see the detailed discussion of alkali metals in^[12]).

We note that the usual methods in which pseudopotentials are used^[5] are from the very outset single-particle methods, and therefore do not make it possible in principle to include consistently the unpaired indirect interion interaction via the conduction electrons.

In the many-particle theory^[1-3], the Coulomb interaction between the electrons and the interaction between the ions are taken into account simultaneously. In particular, the unpaired interaction appears in natural fashion in the terms of third and higher orders in the electron-ion potential. (The paired interaction appears already in the second-order terms.)

Allowance for the terms corresponding to the unpaired interaction turns out to be quite important both from the point of view of the formal theory and for a quantitative analysis of the properties of a metal. Their fundamental role was demonstrated in^[3,13], where it was shown that a number of quantities, for example longitudinal sound, are determined incorrectly in the paired approximation, causing an error even in the terms $\sim (V_K/\epsilon_F)^2$. Explicit allowance for the terms of third and fourth order in the pseudopotential has made it possible to eliminate the fundamental contradictions existing in metal theory.

As to a consistent quantitative analysis of the properties of the metal, it was precisely to this question that the present paper is devoted.

We followed two purposes. First, within the framework of the same scheme, using the same effective electron-ion potential and involving no additional parameters, we aimed at analyzing a wide class of properties

of static and oscillating metal lattices. We investigated the following properties: binding energy, elastic moduli, their dependence on the pressure, the equation of state, the binding energy and stability of different competing modifications, and also the phonon spectrum for a number of symmetrical directions of the wave vector.

In all the calculations we included terms of third order in the pseudopotential, since it is these that are of particular importance and are singled out because of the appreciable cancellation of the contributions from the second-order terms and from the ion lattice^[2]. (Terms of higher orders are much less important in most cases, and their relative magnitude varies from metal to metal.) A quantitative analysis of the role of the third-order terms in the pseudopotential and of their contribution to the entire aggregate of physical quantities was the second purpose of this investigation. (A preliminary analysis of the contribution of $E^{(3)}$ to some quantities was carried out in^[14] for metallic tin.)

The entire analysis is carried out with metallic magnesium as an example. The presence of a complicated crystal structure (hexagonal with two atoms per unit cell) makes it possible to compare the theory with experiment for a large number of quantities (five elastic moduli, six phonon branches, etc.).

On the other hand, magnesium is also convenient because in it, effects of nonlocality in the scattering of an electron by an ion are apparently small^[15], making it possible to use a purely local model pseudopotential and to avoid complications that have no bearing on the present problem.

2. TOTAL ENERGY OF METAL SYSTEM

The starting point for the determination of all the quantities in a metal is the expression for the energy of the ground state of the electron system in the field of the "fastened" ions (see^[1,2,13]):

$$E = E_i + E_e, \quad (2.1)$$

$$E_e = E^{(0)} + E^{(1)} + E^{(2)} + E^{(3)} + \dots \quad (2.2)$$

Here E_i is the electrostatic energy of pointlike ions placed in a neutralizing homogeneous charge, and E_e is the electron energy, which is sought in the form of an expansion in powers of the pseudopotential of the electron-ion interaction $V_{\mathbf{q}}$ (all the quantities are referred to one atom). Here $E^{(0)}$ is the energy of the interacting homogeneous electron gas, and was calculated by the Nozières-Pines approximation^[16].

For the contributions to the energy from the first- and second-order terms in the pseudopotential, we have the following expressions (for details see^[13,12]):

$$E^{(1)} = bZ / \Omega_0; \quad (2.3)$$

$$E^{(2)} = -\frac{\Omega_0}{2} \sum_{\mathbf{K} \neq 0} |V_{\mathbf{K}}|^2 \frac{\pi(\mathbf{K})}{\varepsilon(\mathbf{K})} |S(\mathbf{K})|^2. \quad (2.4)$$

Here Ω_0 is the volume per atom, $S(\mathbf{K})$ is a structure factor, and b is the non-Coulomb part of the Fourier component of the pseudopotential as $q \rightarrow 0$:

$$V_{q \rightarrow 0} = -\frac{4\pi Ze^2}{q^2 \Omega_0} + \frac{b}{\Omega_0}. \quad (2.5)$$

The polarization operator $\Pi(q)$ and the dielectric constant $\varepsilon(q) = 1 + 4\pi e^2 q^{-2} \Pi(q)$ are approximated in the sense of Hubbard^[17], and to ensure a self-consistent scheme (see^[13]), we used the condition $\Pi(0) = n_0^2 \kappa^{(0)}$, where $\kappa^{(0)}$ is the compressibility of the homogeneous electron gas (for details see^[12]).

The expression for $E^{(3)}$ can be written in the form^[1,13]

$$E^{(3)} = \Omega_0 \sum_{\mathbf{K}_1, \mathbf{K}_2, \mathbf{K}_3 \neq 0} \frac{V_{\mathbf{K}_1} V_{\mathbf{K}_2} V_{\mathbf{K}_3}}{\varepsilon(\mathbf{K}_1) \varepsilon(\mathbf{K}_2) \varepsilon(\mathbf{K}_3)} S(\mathbf{K}_1) S(\mathbf{K}_2) S(\mathbf{K}_3) \quad (2.6)$$

$$\times \Lambda^{(3)}(\mathbf{K}_1, \mathbf{K}_2, \mathbf{K}_3) \Delta(\mathbf{K}_1 + \mathbf{K}_2 + \mathbf{K}_3),$$

where Δ is a delta function describing the momentum conservation law.

Here $\Lambda^{(3)}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3)$ is an irreducible "three-pole" containing the sum of all the diagrams with three lines of the external field and an arbitrary number of lines of the electron-electron interaction. If one of the momenta is equal to zero, the limiting values of this three-pole can be obtained from the exact relation^[3], but to calculate the energy (2.6) it is necessary to know $\Lambda^{(3)}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3)$ in the entire momentum region. We have used for this purpose an approximation corresponding to inclusion of a simple loop diagram^(1,2) and corresponding to the self-consistent-field approximation for $E^{(3)}$:

$$\Lambda^{(3)}(q_1, q_2, q_3) = \frac{2m^2}{3\hbar^4 \pi^2} \frac{q_1^2 q_2^2}{q_1 q_2 q_3} \left\{ \sum_m \cos \theta_m \ln \left| \frac{2k_F + q_m}{2k_F - q_m} \right| \right. \\ \left. - \Delta \left[\frac{\ln |(1 - \Delta A)/(1 + \Delta A)|}{2 \arctg \Delta A} \text{ for } k_F/q_R < 1 \right] \right\}. \quad (2.7)$$

Here

$$A = \frac{q_1 q_2 q_3}{(2k_F)^3} \left[1 - \frac{1}{2} \frac{q_1^2 + q_2^2 + q_3^2}{(2k_F)^2} \right]^{-1} = \frac{\sin \theta_1 \sin \theta_2 \sin \theta_3}{x^3 - x(1 + \cos \theta_1 \cos \theta_2 \cos \theta_3)}$$

$$\Delta = \sqrt{|1 - x^2|}, \quad x = k_F/q_R, \quad \cos \theta_K = -q_K/q_m / |q_m|,$$

q_R is the radius of the circle inscribed in the triangle with sides q_1, q_2 , and q_3 , while k_F is the Fermi momentum. The branch $0 \leq \tan^{-1} x \leq \pi$ was chosen in (2.7).

This expression was obtained by direct integration of the contribution from a ring diagram (see^[1]), and the details of its calculation will be published separately. A similar expression was obtained in^[18] in connection with an analysis of the effective one-electron Hamiltonian.

3. ELASTIC MODULI

Knowing the expression for the energy of the metal in the form (2.1)–(2.7), we can determine the elastic moduli C_{ik} by using the method of homogeneous static deformation. In the case of a metal, this method has a significant advantage over the dynamic determination, which uses the so-called long-wave method, i.e., the determination of the elastic moduli from the sound obtained within the framework of the vibrational problem. Indeed, as shown in^[13], although both methods give the same final result, the determination of the elastic moduli with the same accuracy makes it necessary in the long-wave method to take into account terms of higher order in the expansion in powers of the pseudopotential (always two more terms of the expansion).

The presence of the second atom in the unit cell of

magnesium and its noncubic symmetry give rise to specific difficulties in the homogeneous-deformation method. They are connected primarily with the need for taking into account, besides the "external" deformation, which accounts for the change in the shape of the unit cell, also the "internal" deformation, which is connected with the relative displacement of the sublattices (the latter makes a significant contribution to certain moduli).

Another difficulty is the separation of the compressive strain and of the pure shears, and among the latter the strains that conserve the symmetry of the unit cell. This problem was solved for crystals of arbitrary symmetry^[19]. We present here only the results pertaining to hexagonal close-packed (HCP) lattices.

When determining the elastic moduli, the external deformation is best characterized by six independent parameters γ_α —corresponding to the number of parameters describing the unit cell. These parameters can be determined in terms of their connection with the elements of the usual strain tensor ($u_{\alpha\beta} = \partial u_\alpha / \partial x_\beta$; $\bar{u}_{\alpha\beta} = u_{\alpha\beta} + u_{\beta\alpha}$):

$$\begin{aligned} 1 + u_{11} &= (1 + \gamma_1)^{1/2} (1 + \gamma_2)^{-1/2} (1 + \gamma_3)^{-1/2}, \\ 1 + u_{22} &= (1 + \gamma_1)^{1/2} (1 + \gamma_2)^{-1/2} (1 + \gamma_3)^{1/2}, \\ 1 + u_{33} &= (1 + \gamma_1)^{1/2} (1 + \gamma_2)^{1/2}, \\ u_{23} = \gamma_4, \quad u_{13} = \gamma_5, \quad u_{12} = \gamma_6, \quad u_{32} = u_{31} = u_{21} = 0. \end{aligned} \quad (3.1)$$

From this definition we see immediately that γ_1 describes the relative change of the volume, whereas all the remaining γ_i characterize the pure shear strains which leave the volume unchanged. What is singled out here is the parameter γ_2 , characterizing in uniaxial crystals the change of c/a without a change in the volume and in the symmetry of the unit cell:

$$\gamma_2 = \frac{(c/a)' - (c/a)}{(c/a)} \quad (3.2)$$

(the prime denotes the parameters after the deformation).

The parameters of the "internal" deformation are best chosen to be the relative displacements of the sublattices in the basis of the elementary lattice translations, namely the parameters γ_7 , γ_8 , and γ_9 .

The change of the metal's energy at arbitrary deformation can now be written in the following general form:

$$(E' - E) / \Omega = B_{\gamma_1} + 1/2 B_{\gamma_7 \gamma_7} + \dots \quad (3.3)$$

The constants B_i and B_{ij} are determined directly with the aid of the expression for the energy (2.1)–(2.7). To this end it is necessary to calculate the change in energy upon application of the elementary strains $\gamma_1, \dots, \gamma_6$, which are connected with the change in the shape of the unit cell of the reciprocal lattice, and upon application of the strains γ_7, γ_8 , and γ_9 , which change the structure factor $S(\mathbf{K})$.

The obtained quantities can be used to determine the usual elastic moduli (see^[19]). The first derivatives determine here the "isotropic" pressure B_1 and the "anisotropic" pressure B_2 , corresponding to the change of c/a :

$$B_1 = \frac{1}{\Omega} \frac{\partial E}{\partial \gamma_1} = \frac{\partial E}{\partial \Omega} = -P, \quad (3.4)$$

$$B_2 = \frac{1}{\Omega} \frac{\partial E}{\partial \gamma_2} = \frac{1}{\Omega} \left(\frac{c}{a} \right) \frac{\partial E}{\partial (c/a)}. \quad (3.5)$$

(The remaining B_i , as can readily be seen from symmetry considerations, vanish.) The second derivatives serve to determine the elastic moduli of second order (ρ is the density of the metal):

$$\begin{aligned} B_{11} &= B = 1/9(2C_{11} + 2C_{12} + C_{33} + 4C_{13}), \\ B_{22} &= 1/9(2C_{11} + 2C_{12} + 4C_{33} - 8C_{13}), \\ B_{12} &= 1/9(2C_{13} + 2C_{33} - 2C_{11} - 2C_{12}), \\ B_{33} - (B_{88})^2 / B_{88} &= 1/2(C_{11} - C_{12}), \\ B_{44} = C_{44}, \quad B_{77} = B_{88} &= 1/4 a^2 \rho \omega_a^2(0), \\ B_{99} &= 1/4 c^2 \rho \omega_c^2(0). \end{aligned} \quad (3.6)$$

The obtained relations are given for the case $B_1 = B_2 = 0$, and the general expressions are given in^[19].

We recall that the modulus B_{11} is the compression modulus, B_{12} is mixed, and the remainder are pure shear moduli. It is interesting that the second derivatives with respect to the internal deformations give the squares of the limiting optical frequencies as $q \rightarrow 0$ (ω_c^2 for the polarization of the oscillations along the c axis, and ω_a^2 for the polarization in the basal plane). The mixed derivatives of the energy with respect to the external and internal strains make a direct contribution to the modulus $C_{11} - C_{12}$ and correspond by the same token to the relative rigidity of the sublattices in the diatomic crystal.

4. DETERMINATION OF THE PARAMETERS OF THE MODEL PSEUDOPOTENTIAL

The entire preceding exposition pertained to an arbitrary local pseudopotential which, in particular, can be taken from direct calculations using the quantum-mechanical problem for an isolated ion^[5]. Another possibility is to use the energy levels of the ion, as was done in the Heine-Abarenkov paper^[20] or in Shaw's "optimized" variant^[21]. Such methods have certain attractive features, since they make use of a calculation at the "atomic level" for the determination of the properties of matter in the metallic state. At the same time, the corresponding potentials are not yet sufficiently accurate when it comes to the behavior in a wide interval of momentum transfers. For realistic description of the metal, a particularly important shortcoming of these methods is that they do not ensure the fundamental equilibrium condition $P = 0$ in the metal. At the same time, even slight deviations from this condition result in very large errors in the calculation of most physical quantities.

For the reasons indicated, at the present stage of the research we deemed it most advantageous to use model pseudopotentials whose parameters are determined with the aid of certain static quantities characterizing the entire metal as a whole. In particular, it is necessary to satisfy the equilibrium conditions of the static lattice, of which there are two in the case of a hexagonal lattice (see (3.4) and (3.5)):

$$B_1 = 0, \quad (4.1)$$

$$B_2 = 0. \quad (4.2)$$

In other words, the model potential must ensure a minimum for the total energy of the metal at those values of the unit-cell volume Ω_0 and of the anisotropy ratio c/a which are observed in experiment.

As to the concrete choice of the model pseudopotential, an analysis of the properties of alkali metals^[12] has shown that it is perfectly satisfactory to use a two-parameter expression corresponding, for a potential in coordinate space, to a well at $r < r_0$ and to Coulomb interaction at $r > r_0$. (Such a potential was also used in qualitative estimates by Heine; see, for example,^[7].) In rough form, this potential apparently accounts for the main features of the interaction, but on going to complicated metals, where the structure-dependent part of the energy plays a much more important role, it is important to provide for a more subtle description of the interaction, particularly in the region of the "tail" at large q and in the intermediate region from $q = 0$ to q_0 ($V(q_0) = 0$).

In this connection, we have used the following form of the pseudopotential in the momentum representation; this form is close to the described two-parameter potential^[12]:

$$V(q) = -\frac{4\pi Ze^2}{q^2 \Omega_0} \left\{ \left[(1+U) \cos qr_0 - \frac{U \sin qr_0}{qr_0} \right] e^{-(q r_0)^4} - \beta_2 q^2 f(q) \right\}. \quad (4.3)$$

We have introduced cutoffs here at large q , corresponding to "smoothing" of the well, and a new parameter l associated with it. In addition, we have also introduced the parameter β_2 for the function $f(q)$, which makes it possible to specify independently the behavior at $q = 0$.

The function $f(q)$ is chosen such that $f(0) = 1$ at $q = 0$ and decreases rapidly in a narrow interval of q . Therefore its form is immaterial in the static problem, where summation is carried out over the reciprocal-lattice vectors (only its value at $\mathbf{K} = 0$ is involved), while for the dynamic problem the entire second term operates only for small q , so that the potential (4.3) is in general of the three-parameter type for description of the phonons in the overwhelming region of the phase space. The parameter β_2 is connected in simple fashion with the non-Coulomb part of scattering through zero angle (see (2.5)):

$$b = 4\pi Ze^2 \beta, \quad \beta = \beta_1 + \beta_2, \\ \beta_1 = 1/r_0^2 [3 + 2Uqr_0]. \quad (4.4)$$

We have introduced here the characteristic momentum q_0 , at which the pseudopotential vanishes: $V(q_0) = 0$. It is

connected with the depth of the well U by the following relation:

$$U = \frac{q_0 r_0 \cos q_0 r_0}{\sin q_0 r_0 - (q_0 r_0) \cos q_0 r_0}, \quad (4.5)$$

To determine the parameters of the pseudopotential (4.3), we used, in addition to the two equilibrium conditions, also the pure shear modulus B_{22} , which is determined by the behavior of the pseudopotential in the reciprocal-lattice sites, and the limiting optical frequency at $q = 0$, $\omega_c(q = 0)$. This frequency is exceedingly sensitive to the behavior of the potential at a wave vector equal to the reciprocal-lattice vector $[001]$, which, owing to the vanishing of the structure factor, makes no contribution to the static properties, including the characteristics of the electron spectrum (see the discussion in^[22]). We note that the quantity $\omega_c(0)$ is also determined in the method of homogeneous deformation (see (3.6)).

Thus, to determine the parameters we used the following static and long-wave experimental characteristics: Ω_0 , $(c/a)_0$, B_{22} , and $\omega_c^2(0)$. The potential parameters determined within the framework of the inverse problem are given below:

$$r_0 = 0.5500 \text{ \AA}, \quad q_0/2k_F = 0.7600, \\ l(2k_F)^4 = 0.2050, \quad \beta_2/a_0^2 = 0.1054. \quad (4.6)$$

We used here the following experimental data (they were obtained by extrapolation to $T = 0$):

$$a = 3.1945 \text{ \AA} \text{ [23]}, \quad c/a = 1.6231 \text{ [23]},$$

$$B_{22} = 3.01 \cdot 10^{11} \text{ dyn/cm}^2 \text{ [24]}, \quad 1/4\rho c^2 \omega_c^2 = 26 \cdot 10^{11} \text{ dyn/cm}^2 \text{ [25]}.$$

Figure 1 shows the pseudopotential itself and the experimental points obtained from measurements of the Fermi surface with the aid of the van Alphen-de Haas effect^[15].

5. PROPERTIES CORRESPONDING TO THE STATIC LATTICE OF MAGNESIUM

1. Using the obtained pseudopotential, we were able in accordance with the formulas of Sec. 2 to determine the energy of the ideal and deformed metal, and, by differentiating the latter with respect to the deformation parameters, we were able to find the values of the elastic moduli. The results of the calculations, with indication of the contributions made from the individual terms in the initial representation for the energy, are given in Table I (the connection between $B_{\alpha\beta}$ and the usual elastic moduli C_{ijk} is in accordance with (3.6)).

Table I

	E	$-B_{11} = P$	B_{11}	$B_{11} = B$	B_{22}	B_{12}	B_{44}	$\frac{B_{44} = \rho c^2 \omega_c^2}{4}$	$\frac{B_{22} = \rho c^2 \omega_c^2}{4}$	$B_{22} = B_{44}$	B_{44}	$B_{12} = (B_{44})/B_{22}$
E_1	-2.1524	-6.82	-0.0438	-9.10	5.66	0.015	1.70	2.65	134.5	2.98	2.26	—
$E^{(0)}$	-0.2304	1.62	0	3.56	0	0	0	0	0	0	0	—
$E^{(1)}$	0.6705	6.38	0	12.76	0	0	0	0	0	0	0	—
$E^{(2)}$	-0.0906	-1.94	0.0407	-5.79	-1.19	-0.057	0.90	1.06	-97.7	0.19	-0.93	—
$E^{(3)}$	0.0323	0.77	0.0031	1.95	-1.46	0.007	-0.79	-0.93	-10.9	-1.04	-0.55	—
Sum	-1.7705	0.00	0.0000	3.38	3.01	-0.035	1.81	2.78	26.0	2.13	0.78	1.91
Experiment	-1.7787 ± 0.0060	0.00	0.0000	3.69	3.01	-0.028 ± 0.015	1.84	2.57	26.0	—	—	1.88

Note. The energy is given in Ry/atom and the elastic moduli in 10^{11} dyn/cm².

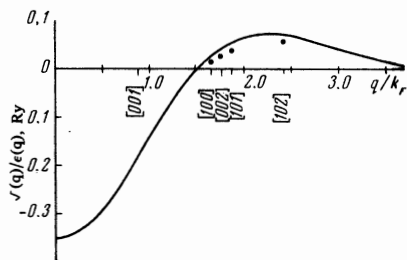


FIG. 1. Pseudopotential of electron-ion interaction in magnesium (the reciprocal-lattice sites and the experimental points from [15] are marked).

Out of the ten quantities given in the table, four (P , B_2 , B_{22} , B_{99}) were used in the determination of the pseudopotential. The remaining six (four elastic moduli, energy, second optical frequency) were determined with the aid of the obtained pseudopotential and serve as a check on the theory. We see that for these quantities the agreement with the experimental data^[24,25] is very good—as a rule within the limits of measurement error. In particular, there is good agreement between experiment and the total energy, the experimental value of which is made up of the cohesion energy^[26] and the energy of double ionization of the magnesium atom^[27] (see the corresponding discussion in^[12]).

2. By varying the volume and using this time a new value of c/a , obtained in accordance with the condition (4.2) (at the same pseudo-potential parameters as before), we can find the equation of state for metallic magnesium (3.4). Figure 2 shows the obtained $\Omega = \Omega(P)$ dependence corresponding to the isotherm $T = 0$. The same figure shows the experimental points obtained in^[28]. We see that there is very good agreement between theory and experiment in a wide interval of pressures. It must be emphasized that this agreement, bearing in mind the complicated character of the structure of magnesium, is far from trivial. We note that the theoretical equation of state for a complicated metal has in fact been obtained here for the first time. The good agreement with experiment, attained both in the case of magnesium and for alkali metals^[12], shows that the scheme is effective for a wide range of pressures.

3. Considerable interest attaches also to an investigation of other crystalline modifications of magnesium, making it possible to determine whether the obtained pseudopotential corresponds to the absolute minimum precisely in a HCP lattice.

The results of calculations for HCP, BCC, and FCC lattices are gathered in Table II. We note first that unlike the existing estimates, in the present paper we have determined for each structure a separate stationary state corresponding to $\partial E/\partial \Omega = 0$, i.e., we obtained the equilibrium volume Ω_0 at which Mg would crystallize in

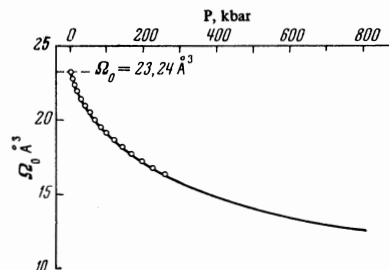


FIG. 2. Equation of state (the experimental points were taken from [28]).

a given type of lattice were it to have the chosen pseudopotential. (It is interesting that the density (Ω_0) changes insignificantly in this case.)

It turned out that a HCP lattice actually has the smallest value of the total energy. It is seen from Table II that BCC and FCC lattices are, in addition, dynamically unstable with respect to pure shear. Thus, the chosen pseudopotential has the required property—it corresponds to preferred crystallization of magnesium in an HCP structure, which is really observed.

4. The good agreement obtained with the experimental results for a wide range of static characteristics of the metal using the same pseudopotential without employing any additional parameters makes it possible to estimate reliably the role of the terms of third order in the electron-ion interaction. This can be done by starting from the data presented in Table I. It is seen from these results that the contribution of $E^{(3)}$ to the energy is small, but is much larger than the energy difference between the different structure modifications of Mg (Tables I and II). This contribution increases rapidly on going over to the pressure and to the compression modulus. In the latter case, owing to the strong cancellation of the contributions from the remaining terms of the expansion in terms of the pseudopotential, the contribution of $E^{(3)}$ is already of the order of the final result. An analogous situation is observed for the contribution of $E^{(3)}$ to other quantities where, as a rule, it is of the same order as $E^{(3)}$ and is the total answer. The only exception is the optical frequency ω_C^2 which, as already indicated, is determined principally by $E^{(2)}$, owing to the large value of the pseudopotential at the nearest site [001].

Summarizing, we can state that the contribution of $E^{(3)}$ is quite significant for the determination of the structure-dependent properties of metallic Mg.

5. Let us see now how the equilibrium parameters of the unit cell arise in this metal. The equilibrium volume (density) is specified by the condition $\partial E/\partial \Omega = 0$. It is easy to see from Table I that a decisive role in the location of this minimum is played by the competition of

Table II. Properties of different modifications

Type of structure	Ω_0 , Å ³	E, Ry/atom	B	$\frac{1}{2}(C_{11} - C_{12})$	C_{44}	B_{22}	B_{33}
BCC	23.2281	-1.76828	3.137	-0.551	3.030	—	—
FCC	23.1728	-1.76942	3.241	-2.376	2.344	—	—
HCP	22.9116	-1.77055	3.382	1.915	1.810	3.005	-0.0353

Note. The elastic moduli are given in 10^{11} dyn/cm².

the terms E_i and $E^{(1)}$. The situation is in general outline the same as in alkali metals^[12]. Although the relative role of the structure-dependent terms increases, the characteristic density arises as before principally because of the volume-dependent isotropic terms (E_i depends little on the concrete configuration of the ion lattice).

The quantity c/a , to the contrary, is the result of competition of only structurally-dependent terms. Figure 3 shows the function $E(\gamma_2)$ for Mg and the contributions from different terms. The parameter γ_2 is defined in (3.2). All the energies are reckoned from their values at $\gamma_2 = 0$.

As seen from the figure, magnesium owes its stability against changes of c/a to the ion energy, which has a minimum at $c/a = 1.6360$, a value very close to the ideal $c/a = \sqrt{8/3} = 1.6330$. It is interesting that $E^{(2)}$ and $E^{(3)}$, to the contrary, have nearby maxima. However, the curvature corresponding to these contributions (it is determined by the value of B_{22}) is much smaller than the curvature of $E_i(\gamma_2)$ and a minimum close to the minimum of $E_i(\gamma_2)$ is produced. The figure shows also the parabola (dotted curve) corresponding to the curvature at the point $\gamma_2 = 0$, from which we see that $E(c/a)$ retains a parabolic character within a 10–20% variation of c/a .

Another interesting characteristic for an anisotropic metal is the average pressure produced at a constant volume as a result of the change of c/a . It is connected with the fact that its individual components depend in different manners on c/a and cancel each other exactly only at $\gamma_2 = 0$. This dependence is also shown in Fig. 3. In principle, it follows from the expansion (3.3) that

$$P(\gamma_2) = -\frac{1}{\Omega} \frac{\partial E}{\partial \gamma_2} = -B_1 - B_{12}\gamma_2 + \dots = -B_{12}\gamma_2 + \dots$$

However, as seen from Table II, the value of B_{12} for Mg

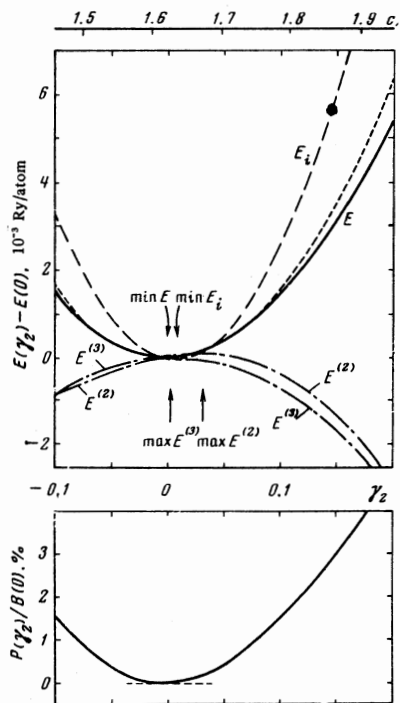


FIG. 3. Dependence of the energy on the deformation γ_2 (on the change of c/a).

is anomalously small and, accordingly, linear behavior is realized in a very narrow interval.

Although the inverse problem has not been solved for other hexagonal metals, qualitative conclusions with respect to c/a can be drawn on the basis of calculations with the Abarenkov-Heine potential (details will be published). In Be, the curvature of $E^{(2)} + E^{(3)}$ as a function of γ_2 is positive and is smaller by an approximate factor of 20 than the curvature corresponding to the ion contribution, so that the minimum is determined by the latter and c/a is close to ideal. In Zn, the curvature of the electron contribution is negative and is of the same order as the curvature of the ion contribution. In this situation, the position of the minimum of the total energy depends strongly on the position of the minimum of E_i and of the maximum of E_e . Accordingly, the experimental value of c/a is shifted by 12% in comparison with the ideal value.

6. In concluding this section, we also present curious results of the calculation of the elastic properties of magnesium under pressure. They are given in Table III in the form of the derivative of the elastic moduli with respect to the average distance, and correspond already to the third derivative with respect to the energy. The calculation was carried out within the framework of the same scheme and was compared with the experimental data borrowed from^[29]. The agreement between theory and experiment should be regarded as good. (The experiment pertains to room temperature and the calculation to $T = 0^\circ\text{K}$.)

6. PHONONS IN MAGNESIUM

1. A quantitative analysis of the phonon spectrum in Mg and its comparison with experiment are of particular interest.

The point is that the static properties of the metal, which were referred to above, are determined by the value of the pseudopotential only at discrete points corresponding to the reciprocal lattice points (see (2.4) and (2.6)). At the same time, for an analysis of the phonon spectrum in the entire momentum interval it is necessary to have a pseudopotential in the entire region of q . Therefore a comparison of theory with experiment is a most serious verification of the entire scheme. Furthermore, the pseudopotential was determined using experimental information corresponding only to long-wave properties of the metal, and an analysis of the results should answer the question as to whether it is possible in this case, i.e., without introducing any additional parameters, to describe the behavior of a complicated phonon spectrum at arbitrary momenta.

2. A detailed theoretical description of the phonon spectrum of Mg was obtained in^[22] on the basis of the scheme employed by us earlier for phonons in metallic tin^[1,2]. This scheme was based on the same physical premises as the scheme employed in the present paper,

Table III

	$d \ln C/d \ln r$				
	C_{11}	C_{33}	C_{44}	$1/2(C_{11} - C_{12})$	$C_{11} + C_{12} + 2C_{33} - 4C_{44}$
Theory	-13.1	-13.8	-12.0	-11.0	-12.9
Experiment [29]	-10.6	-12.1	-9.9	-8.4	-11.6

but it was not fully microscopic, since it considered terms corresponding to $E^{(3)}$ (and higher orders) phenomenologically, with the aid of parametrization of the unpaired interaction in "direct" space. In a number of later papers^[30-33,25] an attempt was made to describe the phonon spectrum of Mg on the basis of only second-order terms $E^{(2)}$ using pseudopotentials of different forms (local and nonlocal). In some of them, the "adjustment" parameters were the effective mass and the charge of the electron. (In^[25] they duplicated exactly the scheme of our paper^[22].) Therefore the present paper, in which the contribution of $E^{(3)}$ to the dynamic matrix of the oscillations is calculated in explicit form, is in this sense of fundamental significance.

3. The dynamic matrix of the oscillations can be represented in the following form^[1-3]:

$$D_{ss'}^{\alpha\beta}(\mathbf{q}) = D_{ss'}^{\alpha\beta}(\mathbf{q}) + D_{2ss'}^{\alpha\beta}(\mathbf{q}) + D_{3ss'}^{\alpha\beta}(\mathbf{q}) \quad (6.1)$$

(α and β are Cartesian indices, while s and s' number the atoms in the unit cell).

The first term yields the contribution made to the dynamic matrix by the ion lattice, and is calculated in the usual manner with the aid of the Ewald transformation. The remaining two describe the electron contributions of the second and third orders in the pseudopotential, respectively ($1-3$). It is convenient to introduce the following symbols for each of the terms in (6.1):

$$D_{ss'}^{\alpha\beta}(\mathbf{q}) = \bar{D}_{ss'}^{\alpha\beta}(\mathbf{q}) - \delta_{ss'} \sum_{s''} \bar{D}_{ss''}^{\alpha\beta}(0). \quad (6.2)$$

Then

$$\begin{aligned} \bar{D}_{2ss'}^{\alpha\beta}(\mathbf{q}) = & -\frac{\Omega_0}{2M} \sum_{\mathbf{K}} (\mathbf{q} + \mathbf{K})^\alpha (\mathbf{q} + \mathbf{K})^\beta |V_{\mathbf{q}+\mathbf{K}}|^2 \\ & \times \exp\{i\mathbf{K}(\rho_s - \rho_{s'})\} \frac{\pi(\mathbf{q} + \mathbf{K})}{\varepsilon(\mathbf{q} + \mathbf{K})}, \end{aligned} \quad (6.3)$$

$$\begin{aligned} \bar{D}_{3ss'}^{\alpha\beta}(\mathbf{q}) = & \frac{3\Omega_0}{M} \sum_{\mathbf{K}_1, \mathbf{K}_2, \mathbf{K}_3} (\mathbf{q} + \mathbf{K}_1)^\alpha (\mathbf{q} + \mathbf{K}_2)^\beta \frac{V_{\mathbf{q}+\mathbf{K}_1} V_{-(\mathbf{q}+\mathbf{K}_2)} V_{\mathbf{K}_3}}{\varepsilon(\mathbf{q} + \mathbf{K}_1) \varepsilon(\mathbf{q} + \mathbf{K}_2) \varepsilon(\mathbf{K}_3)} \\ & \times \Lambda^{(3)}(\mathbf{q} + \mathbf{K}_1; -\mathbf{q} - \mathbf{K}_2; \mathbf{K}_3) S(\mathbf{K}_3) \exp\{i(\mathbf{K}_1 \rho_s - \mathbf{K}_2 \rho_{s'})\} \Delta(\mathbf{K}_1 - \mathbf{K}_2 + \mathbf{K}_3). \end{aligned} \quad (6.4)$$

The three-pole $\Lambda^{(3)}(q_1, q_2, q_3)$ is determined by (2.7), and for the pseudopotential $V(\mathbf{q})$, as above, we used expression (4.3) with the parameters (4.6).

The phonon frequencies were determined in the usual manner by diagonalizing the dynamic matrix (6.1). The calculations were carried out for three symmetrical directions of the wave vector in the Brillouin zone (for the notation see^[22]). We used the lattice parameters corresponding to room temperature, at which the experiment was performed ($a = 3.2094 \text{ \AA}$, $c/a = 1.6235$).

The obtained dispersion curves are shown in Fig. 4, together with the experimental data obtained from neutron scattering^[34-36]. (They were taken from^[25], where a summary of all the measurements is contained.) The upper figure corresponds to polarization of the oscillations along the c axis, and the lower figure corresponds to polarization in the hexagonal plane. The agreement with the experiment should be regarded as exceedingly good. Indeed, the choice of the pseudopotential parameters (see Sec. 4) ensured directly the correct value only for the limiting optical frequency $\omega_c(\mathbf{q} = 0)$ and for

one combination of the transverse sound velocities (B_{22}). A description of the complicated behavior of the six branches of the oscillations in the entire phase space did not require introduction of additional parameters.

4. As already indicated, it is of considerable interest to analyze the role of the terms of third order in the pseudopotential. Figure 5 shows, together with the final curves (solid lines), also the phonon dispersion curves calculated without inclusion of the term D_3 (dashed). The contribution of the third-order terms can be seen to be quite appreciable, and its absence would violate the excellent agreement with experiment. This is shown more clearly in Table IV, which lists the values of the squares

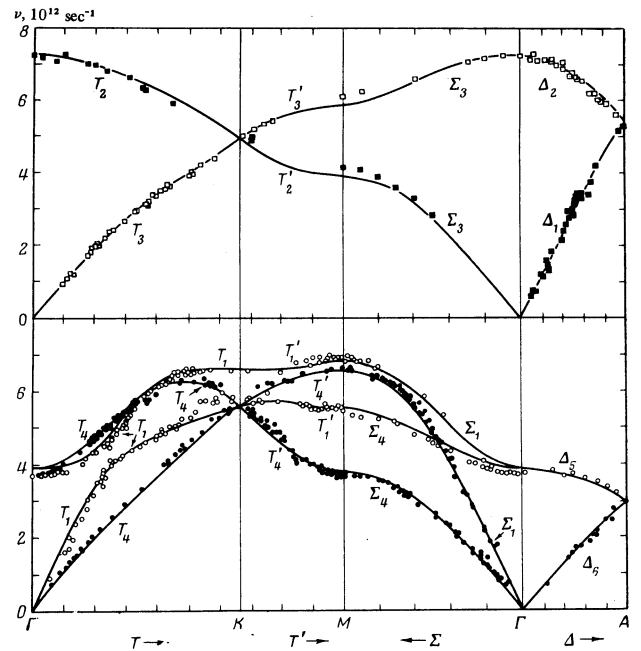


FIG. 4. Phonon dispersion curves (the experimental points were taken from^[25]).

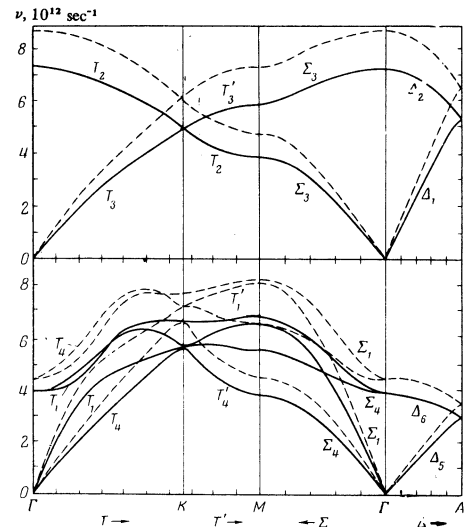


FIG. 5. Individual contributions to the phonon frequencies (solid curve—summary frequencies, dashed—without allowance for the third-order terms).

Table IV. Squares of the frequencies in units of the plasma frequency ω_0

	$(\omega/\omega_0)^2$									
	Γ_1^+	Γ_2^+	A_1	A_2	M_1^-	M_2^+	M_3^+	M_2^-	M_3^-	M_4^+
D_i	0.9061	0.0469	0.9536	0.0232	0.3140	0.1188	0.8368	0.5237	0.1622	0.0443
$D_i + D_3$	0.2386	0.0641	0.1356	0.0375	0.1679	0.0704	0.2131	0.2056	0.1378	0.0642
$D_i + D_2 + D_3$	0.1686	0.0480	0.0920	0.0268	0.1085	0.0477	0.1466	0.1344	0.0958	0.0462

Note. $\omega_0 = 111.1938 \times 10^{12}$ rad/sec.

of the frequencies for several characteristic wave vectors on the boundary of the Brillouin zone (the additive contributions are those made to the dynamic matrix (6.1), which is proportional precisely to the squares of the frequencies). (It is easily seen that the contribution made to the phonons by D_3 is, as a rule, several times smaller than the contribution of D_2 , but owing to the strong mutual cancellation of D_1 and D_2 , the contribution from D_3 becomes already of the order of the final answer. This situation was already discussed qualitatively in^[2,22]. We note also that the scale of the third-order terms obtained in the present paper coincides with that determined phenomenologically in^[22] within the framework of the inverse problem.

CONCLUSION

1. The detailed quantitative analysis of a large group of metallic properties, presented in this paper with magnesium as an example, has demonstrated the effectiveness of the previously developed theoretical scheme.

It is important that the pseudopotential of the electron-ion interaction (which is the only unknown quantity) was determined from very simple and experimentally easily observed properties of the metal, namely the unit-cell parameters and two long-wave characteristics. The subsequent calculation was carried out without additional parameters and has made it possible to describe such subtle properties of the metal as the equation of state, the derivatives of the elastic moduli with respect to the pressure, and the phonon spectrum in the entire region of phase space. In most cases, the agreement with experiment lies within the limits of the experimental error. We also deem it important that the employed potential satisfies the fundamental conditions of equilibrium of the static lattice. This, in particular, corresponds to the absence of stresses in the metal and to an automatic satisfaction of the conditions of Born and Huang (see the discussion in^[22]).

2. As shown by direct calculation, the contribution of the terms of third order in the pseudopotential to the considered metallic properties is quite appreciable. This demonstrates the inadequacy of the customarily employed approximation, corresponding to the inclusion of only second-order terms in the consistent perturbation theory. Allowance for nonlocality of the individual interaction of the electron with the ion (which in principle is easy in our scheme, if necessary), cannot, of course, change this conclusion.

¹E. G. Brovman and Yu. Kagan, Zh. Eksp. Teor. Fiz. 52, 557 (1967) [Sov. Phys.-JETP 25, 365 (1967)].

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

³E. G. Brovman and Yu. Kagan, Zh. Eksp. Teor. Fiz. 57, 1329 (1969) [Sov. Phys.-JETP 30, 721 (1970)].

⁴J. Gallaway, Energy Band Theory, Acad. Press, 1964.

⁵W. Harrison, Pseudopotentials in the Theory of Metals, Benjamin, 1966.

⁶J. M. Ziman, Adv. Phys. 13, 89, 1964.

⁷V. Heine and D. Weaire, Phys. Rev. 152, 603, 1966.

⁸D. Weaire, J. Phys., C, 1, 210, 1968.

⁹C. S. G. Cousins, J. Phys., C, 2, 765, 1969.

¹⁰N. W. Ashcroft and D. C. Langreth, Phys. Rev. 155, 682, 1967.

¹¹R. W. Shaw, J. Phys., C, 2, 2335, 1969.

¹²E. G. Brovman, Yu. Kagan and A. Kholas, Fiz. Tverd. Tela 12, 1001 (1970) [Sov. Phys.-Solid State 12, 786 (1970)].

¹³E. G. Brovman, Yu. Kagan and A. Kholas, Zh. Eksp. Teor. Fiz. 57, 1635 (1969) [Sov. Phys.-JETP 30, 883 (1970)].

¹⁴E. G. Brovman and G. Solt, Solid State Comm. 18, 903, 1970.

¹⁵J. C. Kimball, R. W. Stark and F. H. Mueller, Phys. Rev. 162, 603, 1967.

¹⁶D. Pines and P. Nozieres, Theory of Quantum Liquids, Benjamin, 1966.

¹⁷J. Hubbard, Proc. Roy. Soc. 240, 539, 1967.

¹⁸P. Lloyd and A. Sholl, J. Phys., C, 1, 1620, 1968.

¹⁹E. G. Brovman, Yu. Kagan and A. Kholas, Fiz. Tverd. Tela (1971) (in press).

²⁰V. Heine and I. Abarenkov, Phil. Mag. 9, 451, 1964.

²¹R. W. Shaw, Phys. Rev. 174, 769, 1968.

²²E. G. Brovman, Yu. Kagan and A. Kholas, Neutron Inelastic Scattering (Proc. Symp. Copenhagen), Vol. 1, IAEA, Vienna, 1968, p. 165; Fiz. Tverd. Tela 11, 896 (1969) [Sov. Phys.-Solid State 11, 733 (1969)].

²³H. B. Pearson, A Handbook of Lattice Spacings and Structure of Metals and Alloys, Pergamon Press, 1958.

²⁴I. J. Slutsky and G. W. Garland, Phys. Rev. 107, 972, 1957.

²⁵A. Pindor and R. Pynn, J. Phys., C, 2, 1037, 1969.

²⁶M. Kh. Karapet'yants and M. L. Karapet'yants, Osnovnye termodinamicheskie konstanty neorganicheskikh i organicheskikh veshchestv (Fundamental Thermodynamic Constants of Inorganic and Organic Compounds), Khimiya, 1968.

²⁷Handbook of Chemistry and Physics, 49-th ed., The Chemical Rubber Co., 1968.

²⁸M. G. Drickamer, Solid State Physics, 17, Academic Press, 1965.

²⁹R. E. Schmunk and C. S. Smith, J. Phys. Chem. Sol. 9, 100, 1959.

³⁰T. Schneider and E. Stoll, Neutron Inelastic Scattering (Proc. Symp. Copenhagen), 1, IAEA, Vienna, 1968, p. 101.

³¹R. W. Shaw and R. Pynn, J. Phys., C, 2, 2071, 1969.

³²G. Gilat, G. Rizzi and G. Cubbioti, Phys. Rev. 185, 971, 1969.

³³S. Prakash and S. K. Yoshi, Phys. Rev. 1, 1468, 1970.

³⁴P. K. Yengar, G. Venkataraman, P. R. Vijayarag-

havan, and A. P. Roy, Inelastic Scattering of Neutrons (Proc. Symp. Bombay), 1, IAEA, Vienna, 1965, p. 153.

³⁵G. L. Squires, Proc. Phys. Soc. 88, 919, 1966.

³⁶R. Pynn and G. L. Squires, Neutron Inelastic Scattering (Proc. Symp. Copenhagen), 1, IAEA, Vienna, 1968, p. 215.

Translated by J. G. Adashko

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