Theory of melting of the alkali metals

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The methods of theories of pseudopotentials and simple liquids are used to carry out quantitative computations of the melting characteristics of the alkali metals. A previously described pseudopotential model, the thermodynamic perturbation theory in the Weeks-Chandler-Andersen (WCA) form for a liquid, and the quasiharmonic perturbation theory for the solid phase are employed. The u ≤ 20% compression region, which corresponds to the region of applicability of the WCA method, is considered. For Na, K, Rb, and Cs the theory describes the thermodynamics of the solid and liquid phases with a high degree of accuracy, and the computed melting points \( T_m(u) \) agree with experiment to within 1–2%. The values of the volume jumps \( \Delta V \) for \( u \geq 0 \) are also quite close to the observed values, although the disagreement between \( \Delta V \) and experiment increases with increasing \( u \). The melting entropies \( \Delta S(u) \) exceed the observed values by 15–20%. The possible causes of the deviation of the \( \Delta V(u) \) and \( \Delta S(u) \) values from the experimental data are discussed. For Li the agreement between the computations and experiment is worse because the pseudopotential model used is less adequate. The role of the various contributions to the thermodynamics of melting, the influence on the \( T_m(u) \) of the quantum effects in the liquid phase, the sensitivity of the results to the approximations of the theory, the satisfiability of the Lindemann criterion on the melting curves, etc., are considered.

I. INTRODUCTION

The development of the theory of melting is one of the fundamental problems of the physics of the condensed state. But in spite of the availability of detailed experimental information\(^1,2\) in broad ranges of pressures \( p \), quantitative theories of melting have as yet not been developed even for the simplest materials. The absence of microscopic theories, which is due first and foremost to the absence until very recently of quantitative theories of the liquid state, led to a significant extension to the problem in question of model or phenomenological approaches, such as the "lattice-vacancy,"\(^3,4\) the "topological" and "dislocation,"\(^5,6,7\) and the "quasicrystalline"\(^8,9\) theories of melting. But the microscopic sense of the concepts used in these investigations to describe the liquids does not seem to be quite clear.

Attempts at the development of a more consistent approach to the description of melting were made it impossible to obtain quantitative agreement to within 1–2%. The simplest model systems with pair interaction potentials \( \phi(r) \) of the type of the potential \( \phi_{H} \) for hard spheres, or with power-law potentials \( \phi(r) \propto r^{-12} \), the systems that were mostly considered\(^10,11\) of the realistic \( \phi(r) \) potentials the one that has received the greatest attention is the Lennard-Jones-Jones-type potential

\[
\phi(r) = 4\epsilon [ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} ]
\]

which has been discussed in application to argon.\(^12,13\) The results obtained by computer modeling\(^14\) describe well the data on the melting of argon in the compression range from 0 to 20%, and Hansen and Verlet's\(^15\) construction of the \( P-T \) phase diagram for argon, which is in good agreement with experiment, is considered by a number of authors as "undoubtedly the principal achievement of statistical mechanics" in the explanation of the phase relations between the solid, liquid, and gas.\(^16\)

But the procedures used in computer modeling (sometimes called computer experiments)\(^17\) are extremely long and laborious, have errors that are difficult to estimate,\(^11,13\) and are not very suitable for, for example, the computation of the second derivatives of the thermodynamic potentials. The development of analytic theories of real liquids and melting seems to be desirable.

The development of thermodynamic perturbation theories (PT) for the description of the liquid state\(^18,19\) and of pseudopotential techniques for the computation of the interactions in nontransition metals (see, for example, Ref. 16) has created the prerequisites for the development of a theory of melting for these metals. The first investigations in this direction were performed by Stroud and Ashcroft\(^17\) and Jones.\(^16\) But, as discussed in Ref. 13, the methods and models used in Refs. 17 and 18 are too crude for quantitative computations of the thermodynamics of melting to be possible, and the agreement with experiment obtained for some quantities is only a consequence of a random mutual cancelation of the various errors. Thus, the values obtained in Ref. 17 for the melting points \( T_m(p) \) of sodium in the pressure range from 0 to 30 kbar differ from the observed values 370 < \( T_m \) < 510 K only by 20–90 K. But the refinement of only one of the computed approximations in Ref. 17 should shift \( T_m(p) \) by 200–2000 K.\(^20\) In Jones's paper,\(^16\) on the other hand, the computations are carried out with great care. But the use of quite an inaccurate pseudopotential model and the crudeness of the methods used to describe both the solid phase (the Einstein model) and the liquid (variational method with a basis system of hard spheres, called below the BHS method)\(^11\) made it impossible to obtain quantitative results in Ref. 18, too. Thus, the values obtained at \( p = 0 \) for the heat of transition \( q_m \) in Li, Na, K, and Al differ from
experiment by a factor of 1.5, while the values obtained for the volume jump differ from the experimental values by factors of 2 to 3, and the satisfactory agreement of the computed $T_m$ with experiment (to within 10–20%) is, apparently, also accidental (see Ref. 13 and below).

Recently, Holian et al.\textsuperscript{1,2} computed the thermodynamics of melting of Na, using the methods of molecular dynamics. A rather crude pseudopotential model was used, and the accuracy of the description of the thermodynamics of the solid and liquid phases was not high in each case\textsuperscript{13}; the computed $T_m$ values differ from the experimental values by 10–20%.

The consistent computation of the thermodynamics of melting of real materials clearly requires the solution of the following problems:

a) The construction of a fairly adequate model for the interatomic interactions.

b) The microscopic computation of the Gibbs thermodynamic potential $G(p,T) = G(p,T)$ of the solid phase.

c) The microscopic computation of $G(p,T) = G(p,T)$ for the liquid phase.

The melting curve $T_m(p)$ is then found from the equation

$$G(p,T) = G(p,T),$$

(2)

where the characteristics of the melting are found from thermodynamic relations. Let us note here that the ratio of the melting point $T_m$ to the binding energy $E_b$, the primary quantity in the theory, is quite small: $T_m/E_b \approx 0.5$% (Refs. 13, 19, and 20a). Therefore, in order to be able to compute the $T_m$ to within, say, several percent, the relative error made in the computation of each of the quantities $G$, and $T_m$ should not be higher than $10^{-3}$. It is clear that this makes very high demands in respect of the accuracy with which each of the above-listed problems a)–c) must be solved.

For the alkali metals considered below all these problems are solved in Refs. 19–24 and 11–13. It is shown that, with due care and computational consistency, the simple pseudopotential model described in Refs. 19 and 20a provides a very accurate description—usually at the level of the experimental accuracy—of the broadest range of atomic properties of the metals in question (except some properties of Li): the binding energies and the elastic moduli $c_{44}$ at $T = p = 0$, the equations of state $p(T)$ (Ref. 20a); the phonon spectra\textsuperscript{14,21}; the properties of the hcp phases and of the martensitic transitions\textsuperscript{20b}; the specific heat, the thermal vibrations and thermal expansion\textsuperscript{16a,16b}; the temperature and volume dependences of the elastic moduli $c_{44}(T,p)$ (Ref. 22); the anharmonic effects in the lattice dynamics\textsuperscript{20b,20c} and lattice thermodynamics\textsuperscript{20d}; the structural and thermodynamic properties of the liquid phase at all $T$ right down to the vicinity of the critical point\textsuperscript{14,15,22}; etc. The results obtained in these investigations allow us to assume that the model described in Refs. 19 and 20a and the corresponding potentials $\varphi(p)$ (Ref. 12) describe the ion–ion interactions in the alkali metals sufficiently accurately, and that the thermodynamic computations carried out in Refs. 19–23 for the solid phase are quite reliable.

For the computations of the properties of the liquid phase we shall use the thermodynamic perturbation theory (PT) in the form proposed by Weeks, Chandler, and Andersen (WCA).\textsuperscript{14,15} As shown in Ref. 13, the WCA method turns out to be significantly more adequate for the description of liquid metals than the other variants of the thermodynamic PT (including the HSV variant), and, for a given $\varphi(p)$, it allows us to find the thermodynamic potentials to within a few percent of $T_m$.

Thus, we have all the essential prerequisites for quantitative computations of the melting characteristics of the alkali metals, and these computations, can, apparently, serve as a source of information about the microscopic nature of melting in the case of other metals as well.

In Secs. 2 and 3 we describe the methods used to compute the $G(p,T)$ potentials in the solid and liquid phases respectively. In Sec. 4 we present and discuss the results of the computations, carried out by these methods, of the melting characteristics of the five alkali metals from Li and Cs in the compression range from 0 to 20%. We also consider the question of the role of the various contributions (in particular, of the equilibrium lattice defects) in the thermodynamics of melting, the question of the sensitivity of the results to the various approximations made in the description of the liquid phase, the question of the satisfaction of the Lindemann criterion on the melting curves, etc. The principal results are listed in the Conclusion.

2. THE THERMODYNAMIC POTENTIAL OF THE SOLID PHASE

The thermodynamic functions of the solid phase were found with the aid of the methods described in Refs. 20b, 20c, 21, and 22. In view of the above-noted high-computational-accuracy requirement, in doing this we also took into account the various relatively small contributions to $G$: the contributions from the anharmonicity effects and the equilibrium lattice defects\textsuperscript{20a} from the terms of higher order in the thermal expansion,\textsuperscript{20e} from the electronic excitations, etc. The Gibbs potential per atom $G(p,T)$ (the chemical potential) was written in the form

$$G(p,T) = E_n(Q) + F_n(Q) + \varphi(Q) + T_n(Q) + G_{\text{et}}.$$  

(3)

Here $Q = (p,T)$ is the atomic volume, $E_n(Q)$ is the static binding energy (see, for example, Ref. 25), $F_n(Q)$ is the free energy of the phonons in the harmonic approximation, $T_n(Q)$, and $G_{\text{et}}$ are the contributions of the anharmonicity, the electronic excitations, and the lattice defects. The last three terms in (3) are small corrections to the first three terms, and we shall consider these two groups of contributions separately.

The static, harmonic, and quasiharmonic contributions to $G_n$

The quantity $E_n$, the dominant contribution to (3), is found by expanding it in powers of the electron–ion interaction pseudopotential $\varphi(q)$, and can, in the second-order (in $V'$) approximation used here, be written in the form\textsuperscript{14,15}

$$E_n = E_{\text{ic}} + E_{\text{cr}} + E_{\text{pe}} + E_{\text{pe}} + E_{\text{et}},$$

(4)

Here $E_{\text{ic}}$ is the Coulomb interaction energy of the ions in the compensating negative-charge background (the Madelung
term; $E_{\text{pot}}$ is the correction that takes account of the Born-Mayer repulsion of the ion cores; $E^{0}$ is the energy of the homogeneous electron liquid (described by the Nozières-Pines approximation)\(^\text{14}\); $E^{1}$ is the contribution of the non-Coulomb part of $V(q)$, and $E^{(2)}$ denotes the terms of second order in $V$.\(^\text{15}\)

The pseudopotential $V(q)$ is taken in the local form proposed by Anisimov and Heinze,\(^\text{16,17}\) and contains two parameters characterizing the dimension and depth of the ionic core. These parameters for each metal were determined by fitting the computable values of the atomic volume and the shear modulus $\mu_{\text{el}}$ for $T = p = 0$ to the corresponding experimental values,\(^\text{16,17}\) and further considering them to be constant for all $T$ and $p$ in both the solid and liquid phases (the "hard core" model)\(^\text{11,12}\). For Li the model (with a local pseudopotential) is used less accurately than for the other alkali metals, and the properties of Li are described less accurately by the model.\(^\text{17,18}\)

In the $E_{\text{pot}}$ calculations the Born-Mayer interaction constants were taken from Ref. 27. In this case the $E_{\text{pot}}$ values for Li and Na turn out to be negligibly small, and were neglected, but in K, Rb, and Cs, apparently, this correction also effectively describes the contributions of some effects that have not been explicitly taken into account—effects like the polarizability of the ionic cores, the nonlocality of the pseudopotential, etc.\(^\text{17}\)

In computing $\Omega = \Omega (p, T)$ we neglect the contributions of the last three terms in (3),\(^\text{20a}\) and use the quasiharmonic PT described in Refs. 21 and 20c, and corresponding to the expansion of the thermal expansion in powers of the phonon pressure $p_{\rho}$. In the zeroth approximation the volume $\Omega = \Omega (p, T)$ is found from the solution of the static problem:

$$p_{\rho}(\Omega) = -\frac{\partial E_{\text{pot}}}{\partial \Omega} = p.$$\(^\text{(5)}\)

In the harmonic approximation the phonon free energy $F_{\text{ph}}$ and pressure $p_{\rho}$ are given by the well-known formulas:\(^\text{19}\)

$$F_{\text{ph}}(\Omega, T) = T \sum_{\alpha \beta} \ln \left[ \frac{1}{2 \pi} \sqrt{1 - \frac{1}{2} \frac{\partial \mu_{\text{el}}}{\partial \Omega}} \right],$$\(^\text{(6a)}\)

$$p_{\rho}(\Omega, T) = -\frac{\partial}{\partial \Omega} \ln \left[ \frac{1}{2 \pi} \sqrt{1 - \frac{1}{2} \frac{\partial \mu_{\text{el}}}{\partial \Omega}} \right].$$\(^\text{(6b)}\)

Here $\kappa$, $\omega_{\alpha \beta}$ are the polarization, wave vector, and frequency of the phonon, the sum over $\kappa$ stands for and $d k'/8 \pi^{2}$, the integration being performed over the Brillouin zone, $\beta = 1/T$, and the $\gamma_{\alpha \beta} = -\partial \omega_{\alpha \beta}/\partial \Omega$ are the microscopic Grüneisen constants, which can be simply expressed in terms of the dynamical matrix.\(^\text{33}\) The thermal-expansion effects are described in the quasiharmonic PT with the aid of a power series expansion in the parameter

$$u_{\alpha} = p_{\rho}(\Omega_{0}, T)/B_{\alpha}(\Omega_{0}),$$\(^\text{(7)}\)

where $B_{\alpha} = \partial \mu_{\text{el}}/\partial \alpha$ is the static compression modulus. The quantity $u_{\alpha}$ is "literally" the order of the term $T \gamma_{\alpha \beta}$, where $\gamma_{\alpha \beta} = \partial \omega_{\alpha \beta}/\partial \Omega$ is the atomic energy; in the alkali metals we have $u_{\alpha} \approx 0.06$ in the region close to $T_{m}$. Up to terms $-u_{\alpha}^{2}$ the relative thermal expansion is equal to

$$u_{\alpha}^{2} = \frac{1}{2} [\partial (T \gamma_{\alpha \beta})/\partial \Omega]_{\Omega = \Omega_{0}}.$$\(^\text{(8)}\)

Using (8) and the well-known thermodynamic relations, we can write the expansion of the first three terms of (3) in powers of $u_{\alpha}^{2}$ in the form

$$E_{\text{ph}}(\Omega) = F_{\text{ph}}(\Omega_{0}) + p_{\rho}(\Omega_{0}) + G_{\text{el}}(\Omega_{0}, T),$$\(^\text{(9)}\)

where the quasiharmonic correction $G_{\text{el}}$ is given by the expression

$$G_{\text{el}}(\Omega_{0}, T) = -\gamma(\Omega_{0}, T) \alpha^{2} T^{2},$$\(^\text{(10)}\)

and $A = 1 + (d B_{\alpha}/d \alpha)|_{\Omega = \Omega_{0}}$. Accordingly, the contribution of the terms in (9) to the entropy in the quasiharmonic PT has the form

$$S_{\text{el}}(\Omega, T) = S_{\text{el}}(\Omega_{0}, T) + S_{\text{el}}(\Omega, T),$$\(^\text{(11a)}\)

$$S_{\text{el}} = (d S_{\text{el}}/d T)_{\Omega = \Omega_{0}} a_{\alpha}^{2} \alpha^{2} T^{2},$$\(^\text{(11b)}\)

where the expressions for $S_{\text{el}} = (d S_{\text{el}}/d T)_{\Omega = \Omega_{0}} a_{\alpha}^{2} \alpha^{2} T^{2}$ and $(d S_{\text{el}}/d T)_{\Omega = \Omega_{0}} a_{\alpha}^{2} \alpha^{2} T^{2}$ are obtained by differentiating (6a) and (6b) with respect to $T$.

Let us further give the result of the quasiharmonic PT for the Lindeman parameter

$$r_{\alpha} = 3 \left( \frac{\bar{\rho}^{2}_{\alpha}}{\rho^{2}} \right) = 3 \left( \frac{\partial u_{\alpha}}{\partial T} \right) \left[ 1 + \frac{u_{\alpha}}{2} \left( \frac{\rho^{2}}{\bar{\rho}^{2}} \right) \right] + \frac{2}{3} \frac{u_{\alpha}}{2} u_{\alpha},$$\(^\text{(12a)}\)

$$- \frac{\partial^{2} u_{\alpha}}{\partial T^{2}} \left( \frac{\rho^{2}}{\bar{\rho}^{2}} \right) = - \frac{\partial^{2} u_{\alpha}}{\partial T^{2}} \left( \frac{\rho^{2}}{\bar{\rho}^{2}} \right)$$\(^\text{(12b)}\)

where $\bar{\rho}$ is the mean ion mass. The methods used to evaluate the integrals in (6) and (12) the computational errors of which do not exceed $10^{-6\%}$ are described in Ref. 21a.

The anharmonic, electronic, and vacancion contributions to $G_{\text{el}}$

In computing $E_{\text{ph}}$, $F_{\text{ph}}$, and $G_{\text{el}}$ for $\Omega = \Omega (p, T)$, we used the quasiharmonic expression determined by the relations (5) and (8). As noted in Ref. 20a, for the metals under consideration, the anharmonic term $F_{\text{an}}$ in (3) is small compared to $F_{\text{ph}}$ at all $T$, and has the following form in the high-$T$ region in question:

$$F_{\text{an}} = -\frac{1}{2} \left( \frac{\partial \gamma_{\alpha \beta}}{\partial \Omega} \right) P.$$\(^\text{(13)}\)

The quantities with $\partial \gamma_{\alpha \beta}/\partial \Omega$ are computed in Ref. 20a, as shown in that paper, they are very slowly varying functions of $\Omega$. Therefore, in the compression range considered below
we can consider them to be constants, equal to $c/(\Omega)$ for $\Omega(p,T) = \Omega(0,T_m)$.

The electron contribution $F^e_2$ in (3) was assumed to be given by the usual expression $F^e_2 = -\gamma_e T^2/2$. For the constant $\gamma_e$ we used the free-electron value $\gamma_e = \pi^2/2\times m_e^2/(2\times m)$ (where $m_e$ is the electron mass), since, in the high-$T$ region under consideration, the effects of the $\gamma_e$ renormalization by the electron-phonon interaction tend to zero, while the $\gamma_e$ renormalization by the electron-electron interaction and the band effects in the alkali metals is, apparently, slight.\(^{(19)}\)

The thermodynamic contribution of the equilibrium lattice defects (also called the contribution of the "premelting anomalies") is customarily considered to be primarily associated with the contributions in Table I, let us note that the interpretation (14) of the observed $G_{\text{def}}(T)$ in terms of the monovacancies in the alkali (and many other) metals meets with difficulty, leading to discrepancies in the $n_i$ estimates obtained by different experimental methods. Therefore, although the actual nature and functional form of $G_{\text{def}}$ may differ from (14), the numerical values obtained for $G_{\text{def}}$ and $S_{\text{def}}$ are, apparently, sufficiently close to the real $G_{\text{def}}$ and $S_{\text{def}}$ values. But the value of the volume $\Delta V_{\text{def}} = n_i \Omega_{\text{def}}$ of the defects and the form of the dependences $G_{\text{def}}(p), S_{\text{def}}(p), \Delta V_{\text{def}}(p)$ are now more closely tied with the assumption used, and, therefore, the estimates obtained for them are, generally speaking, less reliable.

To illustrate the role of the above-discussed contributions to the thermodynamics of melting, we give in Table I the values, computed for $p = 0$, of the quantities $G_{\text{vac}}$, $F^e_1$, $\Delta S$, and $\Delta V$, and the corresponding entropies $S_{\text{vac}}$, $S_{\text{vac}}^e = S_{\text{vac}} - S_{\text{vac}}^e$, $S_{\text{def}}$, and $S_{\text{def}}^e = S_{\text{def}} - S_{\text{def}}^e$, where $S_{\text{def}}^e$ and $S_{\text{def}}$ were also taken from Ref. 30. The dependence of $S_{\text{def}}$ on the compression $u = 1 - \Omega/\Omega_{\text{vac}}$ was assumed to be linear in each case:

$$S_{\text{def}} = S_{\text{def}}^e + (1 - u)\frac{\partial S_{\text{def}}^e}{\partial u},$$

where the quantities $\delta$ and $\nu$ were also taken from Ref. 30. The $n_i$ estimates obtained for Li are evidently weaker, and we neglected it.

Before discussing the numerical values of the $G_{\text{def}}$ contributions in Table I, let us note that the interpretation (14) of the observed $G_{\text{def}}(T)$ in terms of the monovacancies in the alkali (and many other) metals meets with difficulty, leading to discrepancies in the $n_i$ estimates obtained by different experimental methods. Therefore, although the actual nature and functional form of $G_{\text{def}}$ may differ from (14), the numerical values obtained for $G_{\text{def}}$ and $S_{\text{def}}$ are, apparently, sufficiently close to the real $G_{\text{def}}$ and $S_{\text{def}}$ values. But the value of the volume $\Delta V_{\text{def}} = n_i \Omega_{\text{def}}$ of the defects and the form of the dependences $G_{\text{def}}(p), S_{\text{def}}(p), \Delta V_{\text{def}}(p)$ are now more closely tied with the assumption used, and, therefore, the estimates obtained for them are, generally speaking, less reliable.

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(which, as noted above, are less reliable) are given in this and the other tables presented below after the results for the other metals. The quantities $G$ and $S$ in Table I denote the first, while $G_{\text{qm}}$ and $S_{\text{qm}}$ in Table II denote the second, terms in the formulas (10) and (11b). It can be seen from Tables I and IV and Fig. 2 that at $T=T_m$ the derivative $\Delta G - G_{\text{qm}}/\Delta T = \Delta S_S = 1$. Therefore, the variations (as a result of particular approximations) in the $G$, or $G_{\text{qm}}$, potential are numerically close to the variation in the computed melting point $T_m$. As to the variations $\Delta S$ and $\Delta S_S$, they are directly connected with the variation in the entropy of melting $\Delta S_m$:

$$\Delta S_m = \Delta G - \Delta G_{\text{qm}}, \quad \Delta (\Delta S) = \Delta S_S - \Delta S_m. \quad (18)$$

It can be seen from (18) and Table I that the discarding of any of the contributions under discussion would lead to some reduction in the computed $T_m$ and some increase in $\Delta S$, $T_m$ being much less sensitive to the corrections than $\Delta S$ and the heat of melting $\varphi_{\text{qm}} = T_m \Delta S$. This evidently reflects the well-known variational properties of the thermodynamic potential.13

### 3. THE GIBBS POTENTIAL FOR THE LIQUID PHASE

The quantity $G$, was found from the relation

$$G(p, T) = F(p, T) + \varphi_{\text{qm}}, \quad (19)$$

where $F = F(p)$ is the free energy of the liquid phase and $\Omega = \Omega(p, T)$ is the atomic volume, which was found from the solution to the equation

$$\rho \frac{d}{dp} \rho = -p \frac{d}{dp} \rho \Omega(p, T) = -p. \quad (20)$$

In the temperature region $\Delta E_{\text{ex}}$ under consideration a liquid metal is a two-component system consisting of ions moving in a classical manner (for the quantum corrections, see below) and a degenerate electron liquid screening the Coulomb interaction between the ions. In this case the presence of conduction electrons leads [as in (4) in the case of the solid phase] to the presence in the energy of large structure-independent terms $E_i$ that depend only on the electron density.13,14

In the second-order—in the pseudopotential—model under consideration, the structure-dependent part of the energy can be represented in the form of a sum of ion-ion pair potentials $\varphi(p)$ of the following form15-17:

$$\varphi(p) = \frac{2}{r} + \varphi_{\text{qm}}(r) - \frac{4}{\epsilon} \int d^3 q \varphi(q) e^{i q r}. \quad (21)$$

Here $\varphi_{\text{qm}}(r)$ is the non-Coulomb part of the ion-ion interaction, for which we shall use the Born-Mayer approximation:

$$\varphi(r) = \frac{\alpha}{r} + 4\pi a \delta(r),$$

while $F(q)$ has, in the case of local pseudopotentials $\varphi(q)$, the form

$$F(q) = F_0(q) \Pi(q)/a(q),$$

where

$$\Pi(q) = 1 + 4\pi a^2 \delta(q)/q^2$$

is the dielectric function.

To compute the free energy $F(\Omega, T)$ of a liquid with the potential [21], we use the thermodynamic PT in the WCA form14,17; the application of this method to liquid metals is described in detail in Ref. 13. In all the variants of the thermodynamic PT, the interior potential $\varphi(r)$ is split up into the potential $\varphi_{\text{qm}}(r)$ of the basis system and a perturbation $\varphi = \varphi_{\text{qm}}$ so that the potential energy $\varphi$ can be written as

$$\varphi = \varphi_{\text{qm}} + \varphi, \quad \varphi = \varphi_{\text{qm}} + \frac{1}{2} \sum q_i q_j, \quad \varphi = \varphi_{\text{qm}} + \frac{1}{2} \sum q_i q_j.$$

The expansion of $F$ in powers of $V$ has the form12,32

### TABLE III. Contributions to the free energy of liquid and solid sodium (in K).

<table>
<thead>
<tr>
<th>p, kbar</th>
<th>Liquid</th>
<th>Crystal</th>
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<td>$-\beta \Omega$</td>
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<table>
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<th>$\varphi_{\text{qm}}$ a.u.</th>
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<td>271.4</td>
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<td>145.4</td>
</tr>
</tbody>
</table>

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Here $F_\infty$ is the structure-independent term, which can be written as:

$$
F_\infty(T) = E_0 + F_0^\text{\infty},
$$

and $E_0^\infty$ is the free energy of the auxiliary system of hard spheres (HS) used in the WCA method. The diameter $d_\infty = d$ of these spheres is determined from the condition for the convergence of the expansion of the function $F_\infty$ in (22) in powers of the softness parameter $\xi$ of the potential $\varphi_{ij}(r)$ in (20) to be the most rapid. The configuration parameter $F_\infty^{(1)}$ of $F_\infty$ is approximated by the Carnahan-Starling (CS) formula, which gives quite an exact interpolation of the computer-modeling results for the HS system:

$$
F_\infty = F_\infty^{(1)} + F_\infty^{(2)},
$$

with $F_\infty^{(1)}$ and $F_\infty^{(2)}$ given by:

$$
F_\infty^{(1)} = \frac{3}{2} \ln \left( \frac{MT^2}{4\pi} \right) - 1, \quad F_\infty^{(2)} = F_\infty^{(1)} \left(\frac{d_\infty - d_{\infty}}{d_{\infty}}\right)^2.
$$

Here $F_\infty$ is the free energy of an ideal gas, $M$ is the ion mass, and $\eta = \frac{\pi d^2}{6d}$ is the packing parameter of the HS.

The quantity $F_\infty^{(1)}$ in (25) stands for the contribution of the first order thermodynamic PT in terms of the deviation of $\varphi(r)$ in (24) from the potential $\varphi_{ij}$, and is given by the expression

$$
F_\infty^{(1)} = \frac{1}{2} \int \frac{dx^2}{(x_{ij})^2} \varphi_{ij}(x),
$$

where $x = r/\xi$ and $g_{ij}(x)$ is the radial distribution function of the HS system. As shown in Ref. 13, in actual calculations, it is more convenient to compute the sum of the terms $E_0$ and $F_\infty^{(1)}$ in (26) and (28) as a single quantity, transforming it into a form similar to (4):

$$
E_0 + F_\infty^{(1)} = E_\text{HS} + E_\text{HS}^\text{conf} + E_\text{HS}^{(1)} + U_{\text{HS}}^{(1)}.
$$

Here $E_0(\Omega)$ and $E(\Omega)$ are the same quantities standing in (4) for volume $\Omega$ values corresponding to the liquid phase, while the first, second, and fifth terms correspond to $E_\text{HS}, E_\text{HS}^{(1)},$ and $E_\text{HS}^{(1)}$ in (4), and are obtained from the expression for the solid phase by replacing the lattice sums by integrals with the radial distribution function $\varphi_{ij}(x)$ and the sums over the reciprocal-lattice vectors by integrals over $q$ with the structure factor $S_{\text{HS}}(q)$.

Finally, the last term in (25) corresponds to the linear— in the softness parameter $\xi$— correction for the deviation of $\varphi(r)$ from $\varphi_{ij}$, and has the form:

$$
F_\infty^{(2)} = -12\eta \int \frac{d\Omega^2}{d\Omega} \varphi_{ij}(x)\varphi_{ij}(x),
$$

where $\eta = \frac{\pi d^2}{6d}$ is the packing parameter of the HS.

Thus, the complete expression for the free energy of the liquid phase has the form:

$$
F = E_\text{HS} + E_\text{HS}^\text{conf} + E_\text{HS}^{(1)} + U_{\text{HS}}^{(1)} + F_\infty^{(2)} + F_\infty^{(1)} + \xi^2 F_\infty^{(2)} + \eta^2 F_\infty^{(1)}.
$$

FIG. 1. Melting curves $C_r(U)\text{MPa}(\text{of the alkali metals})$, the relation between the compression $\mu^*$ and the pressure $p$ is indicated in Table V. For clarity of the figure, the results for each heavier metal are shifted by 50 K downwards relative to the results for the lighter metal. The values indicated along the $T$ axis for Na and K should be read as $T = 50$ K, for Rb as $T = 100$ K, and for Cs as $T = 150$ K. The points are experimental points.

FIG. 2. Temperature dependence of the difference $G[T(p,T) - G_0(p,T)]$ for sodium at $p = 0$. The continuous line is the approximation obtained with the aid of the WCA method; the dashed curve, the approximation obtained by the HV method.
The methods used in the computation of the expressions (29) and (30) (with a computational error of the order of \(10^{-6}\%\)) are described in Ref. 13.

Estimates made in Ref. 13 show that, for \(T=I_p\), and \(p>0\), the terms of higher powers in \(\xi\) discarded in (25) are of the order of \(12\%-T_m\), and the neglected terms of higher powers in \(x\) have roughly the same order of magnitude.\(^{13,13}\)

For the alkali metals, \(\xi=0.1\) and \(\eta=0.5\) in the vicinity of \(T_m\), and the present estimate yields \(\Delta G\approx 0.05T_m\).

It is also noted in Ref. 13 that the WCA method is less accurate in the region of large compressions \(w=1-I_p\) \(\rho/\rho_0\geq 0.15\). This is connected with the fact that the values of the packing parameter \(\eta\) of the auxiliary HS system used become too large: \(\eta \geq 0.58\). At the same time the equilibrium HS system crystallizes when \(\eta=0.49\), and the value \(\eta=\eta_{\text{max}}\approx 0.64\) is indeed the highest possible value for random HS packing.\(^{13,13}\)

Therefore, the properties of the auxiliary HS system begin to exhibit (nonphysical) anomalies at the above-indicated large \(\eta\) values, and the accuracy of the WCA method (especially for the volume derivatives of \(F\)) begins to drop.

The role of the various contributions (26)-(30) is illustrated in Table II by the results for liquid sodium on the (theoretical) melting curve \(T_m=I_p\) \((p)\). For the convenience of comparison of the results for the various metals, in this and the next tables and in the figures, instead of the pressure \(p\) we give the melting-curve values of the observed—in the solid phase—compression \(\Delta\eta^m=1-I_p\) \(\rho/\rho_0\), whose connection with \(p\) is indicated in Table V. It can be seen that the dominant contribution to \(F\) is made by the ideal-gas entropy \(\Delta S_p = -\partial F/\partial T\), this allows us to compute the total \(F\) and \(S\) fairly accurately even when the methods we use to describe the thermodynamics are cruder than the WCA method.\(^{13,13}\)

Table III illustrates the above-noted analogy between the expansions (4) and (29) in powers of the pseudopotential in the solid and liquid phases. It can, in particular, be seen that, near \(T_m\) in the liquid, as well as in the crystal, the second-order term \(U_{\text{II}}^{I_p}\) is small compared to \(U_{\text{III}}^{\text{I_p}}\), and \(F^{\text{eff}}\).

Tables II and III also show that the term \(\Delta U_{\text{II}}^{I_p}\) and \(F^{\text{eff}}\) of (22) is not small compared to the terms \(F_m^{\text{I_p}}\) and \(F_{\text{III}}^{\text{I_p}}\) of zeroth order in \(p\). But, as noted in Refs. 33, 9, and 13, the actual convergence of the expansions (22) is much better than what the formal estimates indicate because of the weakness of the fluctuations in the perturbation \(V\) in the case of close-packed basis systems and the smoothness of the function \(\psi(r)\) in the WCA method. Thus, for a liquid with potential (1), near the triple point the deviation of the entire series (22) from the first term \((\psi)_{\text{me}}\) is \(\approx 0.4\%\) (Ref. 33).

In the metals under consideration this would correspond to an error \(\Delta G_{\text{I_p}}\) of a given \(\psi(p)\) of about 5–7 K. The results presented below suggest that this estimate may not be too far from reality.

It can also be seen from Table II that, as the compression \(w\) is increased, the quantities \(F_{\text{III}}^{\text{I_p}} = (\psi)_{\text{me}}\) and \(F_{\text{II}}\) begin to change drastically, and the quantity \((\psi)_{\text{me}}\) even changes sign drastically at high \(w>0.2\). This is due to the sharp increase that occurs at large \(w\) in the first peak of the radial distribution function \(g_{\text{HS}}(r)\) in (28) and (30) for \(\pi \approx 1\) \((g_{\text{HS}}(1))\). It can be expressed in terms of \(P = -\partial F_{\text{I_p}}/\partial T\) as \(g_{\text{HS}}(1)\psi = (g_{\text{HS}} - 1)\psi/\psi\). As has already been noted, these nonphysical anomalies in the properties of the auxiliary HS system lead to a drop in the accuracy of the WCA method in the \(w>0.2\) region. It can, however, be seen that, for moderate \(w < 0.2\), the sum \(F_{\text{III}}^{\text{I_p}} + F_{\text{II}} = (\psi)_{\text{me}}\), varies with a much more slowly than each of the terms, so that the total \(F\), (22), varies smoothly in this region of \(w\).

### 4. MELTING CHARACTERISTICS OF THE ALKALI METALS

The results of the computations of the properties of the alkali metals on the melting curves are shown in Tables I–V.

#### TABLE V. The thermodynamic quantities on the melting curves \(T_m(p)\).

<table>
<thead>
<tr>
<th>Metal</th>
<th>(n)</th>
<th>(\psi_{\text{cr}})</th>
<th>(T_m(n))</th>
<th>(S_m)</th>
<th>(\Delta S)</th>
<th>(\Delta U)</th>
<th>(U_{\text{II}})</th>
<th>(U_{\text{III}})</th>
<th>(S_{\text{III}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>0</td>
<td>0.371</td>
<td>0.343</td>
<td>0.371</td>
<td>0.343</td>
<td>0.371</td>
<td>0.343</td>
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<tr>
<td></td>
<td>0.8</td>
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<td>0.371</td>
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<td>0.343</td>
<td>0.371</td>
<td>0.343</td>
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<tr>
<td>K</td>
<td>0</td>
<td>0.371</td>
<td>0.343</td>
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and in Figs. 1–4. For Na, K, Rb, and Cs all these results turn out to be similar (although the accuracy of the pseudopotential model used drops somewhat as we go from Na to Cs [Refs. 19–24]). Therefore, comprehensive data are given only for Na and Rb. As noted above, our model with a local pseudopotential is less adequate for the description of Li, so that the results for Li are illustrative in character, and are not discussed in detail.

The values of $G^*$ and $G^T$ in Table IV indicate the "thermal" contributions, which can be expressed in terms of the directly measurable enthalpy and entropy: 

$$G^*_F(T) - G^*_F(0),$$

(32)

where $G^*_F(0)$ is the energy of the solid bcc metal at $T = 0$; the theoretical $E_v$ values used are given in Table IV. The experimental values are given in brackets in Tables IV and V. In the case of $G^*$, $G^T$, $S$, and $S_F$ in Table IV these values were taken from Ref. 34; in the case of all the remaining quantities, from Refs. 2 and 31. All the theoretical results in Tables II and IV correspond to the computed $T_m(p)$ values found with a prescribed $\rho$ from Eq. (2).

Let us first discuss the results in Table III, which characterize the accuracy with which the theory describes the solid and the liquid phases separately. In the case of the crystal the quasiharmonic PT formulas (3), (5)–(12) furnish a consistent description of the thermodynamics, and the inaccuracy of the theory [for a given form of the potentials $\rho(\rho)$] may be due only to the relatively small contributions of the type $G_{\text{rad}}$ in (3). Therefore, a comparison with experiment of the quantities $G^*$, $S$, and $\tilde{D}_T$ in Table IV allows us to estimate the effect of the errors of the interaction model itself on the thermodynamics, whereas for the liquid phase the accuracy of the WCA method used is generally speaking, also not quite apparent.\(^{13}\) It can be seen that the results for $S$ and $G^T$ are in good agreement with the results of the phonon-spectrum computations carried out in the same model.\(^{13}\) Thus, for Na the disagreement with experiment, $\Delta S = S_S - S^T$, $\approx -0.17$, which is largely determined by the error made in the computation of $S_S$ (11a), corresponds, in accordance with the results obtained in Ref. 19 for $\omega_{1S}$ in Na, to the error $(\delta \omega_{1S}/\omega_{1S}) = 0.06$ made in the phonon-frequency computations. At the same time, in Rb, where the $\omega_{1S}$'s computed in Ref. 19 are in good agreement with experiment, the $S$ value in Table IV almost coincides with the observed value. Similarly, the discrepancies $\Delta G^T = \delta G^T$ are largely determined by the differences between the errors $\delta S$ and $\Delta G^T + \delta (E^T - T S) = \Delta \omega_{1S}$, where $E_{\text{zpc}}$ is the zero-point-vibration energy. Thus, according to this estimate, $(\delta \omega_{1S}) = 0.08(\omega_{1S})$ in Na. Let us also note that, in the case of Cs, the good agreement between experiment and the quantities $S_S$ and $G^T$ and the specific-heat calculations\(^{12,14}\) shows that the phonon spectra of Cs (not yet measured) are apparently well described by the model used.

The results for the solid and liquid phases in Table IV allow us to conclude that the accuracy of the WCA method used with a given interaction model is markedly higher than the accuracy with which this same model describes the interactions in the metals under consideration, and the errors introduced by the model into the differences $G^T - G^*$ almost cancel out: $\Delta \omega_{1S} = 0$. This makes it possible for us to compute the $T_m(p)$ values with quite a high accuracy (see below). There also occurs significant cancellation of the errors in the computed equilibrium volumes $\tilde{D}_T$ and $\tilde{D}_S$. At the same time the WCA method apparently overestimates slightly the entropy $S_F$, the magnitude of this error $(\delta S_{F,\text{WCA}} - \delta S_F) = 0.13$–0.15 being weakly dependent on the model used (in contrast to the errors $\Delta S_F$ and $\Delta S_S$, which depend essentially on the model).

The Figs. 1–4 and Table V describe the thermodynamics of melting. It can be seen that the computed melting curves of $T_m(p)$ are in excellent agreement with experiment at all not too high compression values $\rho \leq 20\%$. This confirms the above-indicated high accuracy of the WCA method in application to liquids, and the possibility of the use of this method for precision $T_m$ calculations when we have sufficiently adequate models for the interactions. In this case it can be seen that the sensitivity of $T_m$ to the details of the models (e.g., the accuracies with which the phonon spectra are described) is not too high: the melting points $T_m$ for Na and Rb have been computed with practically the same degree of accuracy. At the same time, Fig. 2 and the values for Na (HEF) in Table V show that the use of the now commonly employed HEF method for the computation of $G^T$ leads to the overestimation of $T_m$ by a factor of almost two, and is consequently not suitable for quantitative $T_m$ computations. Therefore, the satisfactory agreement with experiment ob-
tained with the aid of the HSV method in Refs. 19 and 20 for $T_m$ in the alkali metals is apparently due only to accidental cancellation of the errors introduced by the models employed and the methods used to compute $G_0$ and $G_i$ [Ref. 13].

Let us make a remark about the effect on the $T_m$ calculations of the quantum corrections, which we neglected in the liquid (in contrast to the solid) phase. The contribution $G_{\text{q}}$ of this correction in $G_i$ (see Ref. 32, §3) can be estimated by assuming that it has the same value in the solid phase at $T \approx T_m$

$$G_{\text{q}} = G_{\text{q}_0} = \frac{1}{24\pi} \sum \delta u^{(m)} \frac{1}{18\pi} E_{\text{f}_0}^2,$$

where the last estimate corresponds to the Einstein model for the phonon spectrum. Using for $E_{\text{f}_0}$ the values computed in Ref. 21a, we obtain for $G_{\text{q}}$, as in Li, Na, K, Rb, and Cs, the values 28, 6, 2, 1, and 0.5 K, respectively. According to (15), this correction should lead to an increase $\Delta T_m = G_{\text{q}}$, in the computed $T_m$. It can be seen from Tables IV and V that allowance for $G_{\text{q}}$ draws theory and experiment slightly together in Li (yielding $T_m \approx 400$ K for $T_m^{\text{exp}} = 454$ K), and preserves the agreement between $T_m$ and experiment to within 5–10 K for the remaining metals.

Let us discuss the results given in Table IV and Fig. 3 for the volume jump $A = \omega^P / 1 - \omega$, that occurs during the melting. For $p = 0$ the computed $A / \omega$ values agree with experiment to within 2–9%. But if we assume that the volume of the defects is independent of $p$, i.e., if we assume that $\omega_{\text{def}}(p) = \omega_{\text{def}}(0)$, then the computed $A / \omega$ values will be close to the observed values at all compressions $u \leq 0.15$; this is illustrated for Na by the dashed curve in Fig. 3. The description of the entropy of melting $S_m$ gets similarly (though to a lesser extent) refined if we assume that the contribution of the defects is independent of $p$, i.e., if we assume that $S_m(p) = S_m(0)$ (see Fig. 4). The contribution of $G_{\text{def}}$ to $G_i$, is small [see Table I], but even here the assumption that $G_{\text{def}}(p) = G_{\text{def}}(0)$, which lowers $G_i$ and $T_m$, slightly improves the agreement of $T_m(p)$ with experiment at high $p$.

Thus, our results could be an indication of the fact that the premelting anomalies in the metals under consideration are not due to the production of vacancies, but have a different nature. Let us, however, note that this conclusion depends essentially on the values we use in the computations for the quantities $S_m$, $E_m$, and $n_m$ in (14) and (15). Thus, if $n_m$ is in fact much smaller than the value indicated by our estimates (this is apparently indicated by the published $n_m$ measurements$^{19,20}$, and the appreciable magnitude of the anomalies in the specific heat $c_v = (\partial E_v / \partial T)_n$ is accounted for by $S_m$ and $E_m$ values that are much higher than our values, then the contributions of $G_{\text{def}} / \omega$ can be much smaller than the contributions obtained in the above-performed estimates. The theoretical $A / \omega$ values for $p = 0$, shown in Fig. 3, will then become 0.5–0.7% greater than the observed values, and will, with increasing $p$, vary roughly parallel to the experimental curves right up into the region $u \approx 0.15$, where the WCA method becomes inapplicable.

Then our results would indicate that there occurs in the WCA method a systematic, model- and compression-insensitive, 0.5–0.7% overestimation of the theoretical values $D_i$ of the liquid phase. Quantitative computations of the quantities $S_m$, $E_m$ in the alkali metals seem to be quite desirable for the elucidation of these questions.

In Fig. 4 we present the results for the entropy of melting $S_m$. It can be seen, in particular, that the above-noted model-insensitive disagreement between the magnitude of the entropy jump and experiment, $\delta S_m$ = 0.13–0.15, remains roughly constant under pressure if, in accordance with the foregoing, we assume that the entropy of the defects in the solid phase is a slowly varying function of $p$, i.e., that $S_{\text{def}}(p) = S_{\text{def}}(0)$. As has already been noted, this discrepancy in $S_m$ is evidently due to some overestimation of the entropy $S$ in the WCA method, which should give rise to an error $\delta S = - T \delta S_m = - 50$ K in the free energy. Therefore, the above-noted high accuracy of the $G_i$ computations may indicate the cancellation of this error by a similar error in the computed energy $E_i$. But the occurrence of such a cancellation of the errors in the $G_i$ computations carried out by the WCA method.
Finally, let us consider the question, which has aroused great interest, of the "criteria" for melting or crystallization, i.e., the question of the possible constancy of some characteristics of the solid and liquid phases on the melting curves of different materials. For the solid phase the best known is Lindemann's semiempirical rule asserting the constancy of the ratio \( \tau_0 / T_m \), [12a], in crystals with similar types of binding. Our calculations show that, for the alkali metals, this criterion is fulfilled with a high degree of accuracy. At all the investigated compression values \( u \leq 0.2 \) the computed \( r_1(p) \) values on the melting curves lie in the range \( 0.174 < r_1 < 0.181 \), and almost do not vary with \( p [\text{GPa}] / \tau_0 (0) \leq 0.01 - 0.02 \), whereas, for example, the thermal expansion \( u(F) \) computed for \( T = T_m(p) \) from (8) decreases by a factor of 1.5-2. For the liquid phase, Ferraz and March [13] have suggested that the crystallization of simple liquids occurs when the height \( S_p \) of the principal peak of the structure factor \( S(q) \), increasing with decreasing \( T \), attains some value \( S_p \approx 2-3.0 \), which indicates a definite degree of short-range order (see also Ref. 24). Here we note that the configuration entropy \( S_{\text{conf}} \) - \( S_{\text{conf}} \), which determines the deviation of \( S \) from the entropy \( S_{\text{conf}} \) of the ideal gas, can also serve as a qualitative measure of the short-range order in a liquid. In the investigated compression range \( 0 < u \leq 0.2 \) the \( S_{\text{conf}} \) values on the melting curves of the alkali metals are indeed quite close: in experiment the quantity \( S_{\text{conf}} \) increases by 3-4%, while in the computations the variations \( \Delta S_{\text{conf}} \) amount to 1-2%. For the purpose of comparison, let us point out that, when, for example, we heat liquid Na from 371 to 473 K at \( p = 0 \), the quantity \( S_{\text{conf}} \) decreases by \( 15 \%) \), while the peak \( S_{\text{conf}} \) decreases by \( 15 \% \). Therefore, the approximate constancy of \( S_{\text{conf}} \) can be regarded as an indirect indication of the possibility that the criterion that \( S_p \approx \text{const} \) on the melting curves of the alkali metals is fulfilled.

5. CONCLUSION

In conclusion, let us enumerate the main results of the present paper. They can be conditionally divided into methodological and physical results.

The main methodological result is the demonstration of the fact that the WCA method furnishes a highly accurate description of the thermodynamics of liquid metals when we use fairly adequate models for the interactions, as well as the possibility of employing this method for precision computations of \( T_m \) for all moderate compressions \( \approx 0.2 \leq 0.2 \). At the same time is is shown that the accuracy of the now commonly used HSV method is insufficient for quantitative computations of \( T_m \) in metals. Our calculations also indicate that, in the WCA method, the entropy \( S \) of the liquid phase at \( T = T_m \) is overestimated by an amount \( \Delta S \approx 0.5 \) that depends weakly on the compression and the form of the model used. In the free energy \( F \), this error is, however, almost canceled out by a similar overestimation of the energy \( F \).

We have also considered in detail the various thermodynamic contributions to the solid and liquid phases and their role in the thermodynamics of melting. We give, in particular, an estimate for the influence on \( T_m \) of the quantum effects associated with the motion of the ions in the liquid, and show that this influence is fairly appreciable in Li, but weak in the other metals.

The important physical result seems to be the indication that the position of \( T_m \) is relatively insensitive to the form of the models for the interactions, in particular, to the accuracy with which the phonon spectrum is described. This may reflect certain properties of universal melting, at least for materials with similar types of binding, and facilitate the development of quantitative theories of melting. Also important is the result that we cannot describe the observed compression dependence of the volume jump \( \Delta V \) with the use of the "vacancy" expressions (14) and (15) for the contributions \( G_{\text{conf}} \) and \( \Delta G_{\text{def}} = \Delta G_{\text{def}} / \partial p \). As discussed above, this may indicate that the "premelting anomalies" are not due to the production of vacancies, but have a different nature, or that the values of the entropies and energies of formation of the vacancies are much higher than the values obtained in the preceding estimates. It is also noted that the good agreement with experiment of the computed \( G_p \), \( S \), and specific heat in Cs in an indication of the high accuracy of the description of the phonon spectrum of this metal by the model used.

Finally, it is shown that the Lindeman criterion \( r_1 \approx \text{const} \) (where \( r_1 \) is given by (12)) for melting is, apparently, very well fulfilled on the melting curves of the alkali metals, at least in the region of moderate compressions \( u \leq 0.2 \).

On the whole, the results of the present paper show that, in the case of simple metals, the combination of the pseudo-potential theory with the thermodynamic PT in the form of the WCA method allows a quantitative description of the thermodynamics of liquid metals and the thermodynamics of melting.

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