The equation of state of crystalline and liquid alkali metals

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It is shown that the high-temperature, experimental P-V-T data for alkali metals contain information that makes it possible to calculate the zero-compression isotherms for crystalline alkali metals and certain P-V ratios for liquids, which can be interpreted as the zero-compression isotherms of supercooled, liquid alkali metals. It was found that both systems of zero isotherms are almost identical in all cases except lithium.

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For a number of years, we have been investigating the equation of state of solid and liquid alkali metals at pressures up to 20 kbar and temperatures from 20 to 250 °C.[1,2]

As a consequence of an analysis of experimental results, it was established that polynomials of the form

$$P = aT + bT^2 + c\,T/V + \sum_i \alpha_i V^{-i}, \tag{1}$$

where P, V, and T are the pressure, volume, and temperature, respectively, and a, b, c, and α_i are constants for calculation of the experimental data, can be used effectively as an empirical equation of state for crystalline alkali metals at temperatures of the order of and higher than the Debye temperature Θ_D. The rms error of the approximation of the experimental data by polynomials like (1) does not exceed 10 bar, consistent with the *a priori* estimates. It is easy to see that the polynomial (1) agrees with the idea that at temperatures close to the melting point the free energy of an alkali metal can be represented as a sum of two parts, one which represents the ground state energy and the other denotes the thermal energy. The calculations show that the contribution of terms of the form T^2 and T/V to the total pressure is very small, and hence the derivative $(\partial P/\partial T)_V$ changes relatively little with the temperature and pressure, consistent with the theoretical calculations.[3]

Equation (1), therefore is completely reasonable from a physical point of view.

In reality, however, it is not clear whether Eq. (1) with the empirically determined coefficients contains information about the basic equation of state for a material. Investigation of this problem is of considerable interest, since the equation of states for a material at moderate temperatures can be investigated with much higher accuracy than at liquid helium temperature.

Using the Debye model of a solid, we shall first determine the information the high-temperature equation of state can contain about the ground state.

Let us write the energy of the crystal in the Debye approximation:

$$U = U_{st} + (9/8)R\Theta + 3RTf(\Theta/T). \tag{2}$$

The terms of the right-hand side of Eq. (2) are, respectively, the static, zero, and thermal energy.

At $T > \Theta$ the term $3Rf(\Theta/T)$ in Eq. (2) can be represented in the form $3RT - (9/8)R\Theta$ and with allowance for the anharmonic correction for Eq. (2) it becomes

$$U = U_{st} + 3RT + AT^2. \tag{3}$$

It follows from Eq. (3) that

$$P - P_s = P_{st} - (dA/dV)_T T^2, \tag{4}$$

where P_s is the pressure determined by the entropy term in the free energy.

Thus, we can extract from the high-temperature data the information about the static-lattice pressure, if the contributions introduced by the entropy and anharmonic terms are taken into account correctly. However, the information about the contribution of zero vibrations cannot be obtained.

For the equation of state of the the type being considered by us, we can easily see that

$$P - P_s = \sum_i a_i V^{-i} - bT^2 \tag{5}$$

and, consequently,

$$P_{st} = \sum_i a_i V^{-i} \tag{6}$$

Equation (6) can be easily verified, since the experimental data for the compression of alkali metals at 4.2 K are available. In this case the pressure of the zero vibrations must be taken into account, which can be easily done within the context of the Debye model.

A comparison of the results of our calculations and the direct experimental data (see Fig. 1) demonstrates that the experimental isotherms are in very good agreement with the calculated isotherms; this shows that the information about the ground state can be obtained from the experimental data.

Let us now examine the liquid metals. As it turned out, an equation of the form (1) adequately describes the P-V-T data for liquid metals, although Eq. (1) has a purely "solid-state" structure. In addition, an analysis of the experimental data shows that the analogy in the thermodynamic properties of liquid and solid alkali metals can be extended further than the approximating equations. The compressibilities of liquid and solid metals are very similar, and their temperature dependence is very small in both the solid and liquid phases.[1,2]

We emphasize that in the case of condensed noble gases the values of the compressibility and especially its temperature dependence in the liquid phases are much larger than the corresponding values that characterize the solid state (see, for example, Refs. 4 and 5).
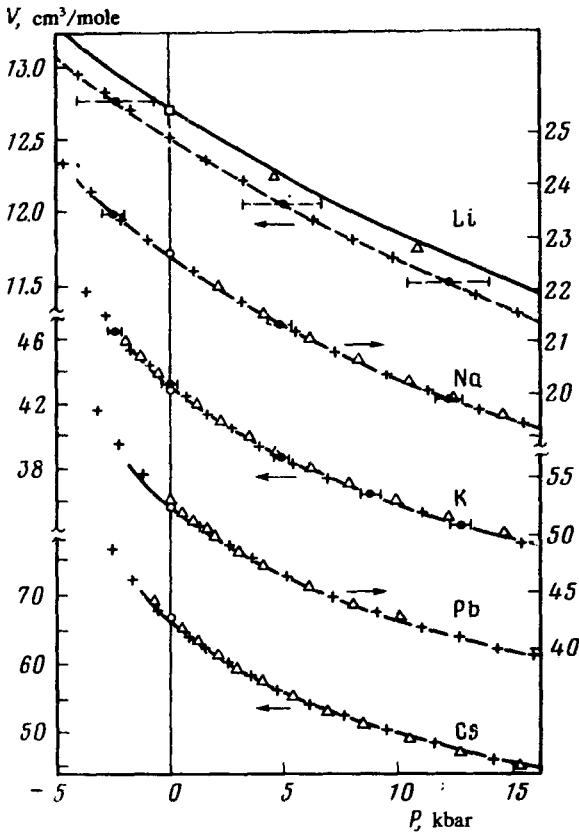
FIG. 1. Equation of state for alkali metals at $T = 0$. The calculation was taken from the high-temperature data: ——, crystal; $+$, "liquid". The calculation errors, not shown on graph, do not exceed 100 bar: $\triangle$, Refs. 7–11; $\square$, Ref. 12; $\bigcirc$, Ref. 13.

We shall assume that the thermodynamics of liquid alkali metals can be constructed exactly the same as the thermodynamics of crystal, i.e., in terms of the ground state and thermal excitations. Thus, the term $P = [\Sigma_i \alpha_i V^{-i}]$, which is separated from the high-temperature equation of state, determines the pressure of the ground state of the "liquid" after the subtractions of the zero-energy contribution, i.e., the pressure P_{st} of a certain static configuration of atoms. By crudely estimating the zero energy of the "liquid" by means of the Debye model, we can compare the zero liquid isotherms with the corresponding crystal isotherms.

As seen in Fig. 1, the "liquid" zero isotherms are identical to the corresponding isotherms of the solid alkali metals, within the accuracy limits of the experiment and the procedure of excluding the temperature terms, in all cases except lithium, where the situation is not completely clear. This rather unexpected result leads to the conclusion that the energies of the corresponding states at $T = 0$ for Na, K, Rb and Cs are either very similar or differ by a constant. In the case of Li, if the observed difference is real, then the "liquid" zero isotherm lies below the zero isotherm of the crystal with respect to pressure and hence, even if the energy of the crystal is lower than that of the "liquid," the compression will contribute to the stability of the "liquid" state at moderate pressure. [1)]

Thus, the results of this paper do not exclude the possibility that the static energies of amorphous alkali metals can have very similar values to those that characterize their crystalline state. In this case the most stable state of the alkali metal at $T = 0$ is determined by the corresponding zero energies.

In light of the results of this paper, the nature of the maximum on the cesium melting curve[6] should be analyzed again. In particular, if the assumption that the energy of the "liquid" is similar to that of the crystal in the ground state is confirmed, then we can propose a mechanism that changes the sign of the volume jump as a result of melting the cesium without the s-d transition.

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[1]The observed difference in the zero isotherms and "liquid" lithium may be due to the fact that the condition of classical behavior $T \succ \Theta_D$ is not satisfied in this case.

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