The dissolution of the vacancy gas in solids and high pressure phase transitions

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Abstract

The formula for the number density of vacancies in a solid under pressure is obtained. The mean number density of vacancies in a solid under stress or tension is also estimated. The dissolution of the vacancy gas in solids is shown to be responsible for the phases with composite incommensurate structures in metals under high pressure and also for the low values of the elastic limit and tensile strength of solids.

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In the last decade, the phases with composite incommensurate structures have been discovered in metals and some other elemental solids under high pressure [1-3] (for a review see Ref. 4). Similar phenomenon is the decrease of the melting temperature of sodium under pressure [5]. All these effects can be explained by the dissolution of the vacancy gas in solids under pressure following from the thermodynamic consideration.

According to the thermodynamic equation [6]

\[ dE = TdS - pdV, \]  

(1)

where \( E \) is the energy, \( T \) is the temperature, \( S \) is the entropy, \( p \) is the pressure, and \( V \) is the volume of a solid, the energy of a solid increases with pressure, so the pressure acts as the energy factor similarly to the temperature. Therefore, the number of vacancies in a solid increases both with temperature and with pressure.

Consider at first the dissolution of the vacancy gas in solids at ambient pressure. We treat the dissolution of vacancies in a solid as a phase transition (the evaporation of vacancies from the ‘condensed phase’ at the surface of the solid) and apply the Clausius-Clapeyron equation [6] in the form

\[ \frac{dP}{dT} = \frac{E_v}{Tv}, \]  

(2)

where \( E_v \) is the energy of the vacancy formation, \( v \) is the volume per one vacancy, and the pressure of the vacancy gas in a solid is given by the formula

\[ P = nT = T/v, \]  

(3)

where \( n \) is the number density of vacancies. Here the Boltzmann constant \( k_B \) is included in the definition of the temperature \( T \).

From equations (2) and (3) we obtain

\[ n = \left( \frac{P_0}{T} \right) \exp \left( -\frac{E_v}{T} \right) = \left( n_0T_0/T \right) \exp \left( -\frac{E_v}{T} \right), \]  

(4)

where \( P_0 = n_0T_0 \) is a constant, \( T_0 \) can be put equal to the melting temperature of the solid at ambient pressure, and the constant \( n_0 \) has an order of magnitude of the number density of atoms in the solid.
The obtained formula (4) describes the thermal expansion of the solid. It should be taken into account that the dissolution of the vacancy gas in a solid causes the deformation of the crystalline lattice and changes the lattice parameters.

The energy of the vacancy formation depends on the temperature and pressure, the first terms of the corresponding series expansion having the form

\[ E_v = E_0 - cT - \alpha P/n_0, \]  

(5)

where \( c \) and \( \alpha \) are dimensionless constants. The temperature dependence of \( E_v \) in the equation (5) causes only the change of a constant \( P_0 \) in the equation (4). The effect of the pressure dependence of the energy of the vacancy formation is much more essential. On the atomic scale, the pressure dependence of the energy of the vacancy formation in the equation (5) is produced by the strong atomic relaxation in a crystalline solid under high pressure. Note that we do not consider here the comparatively narrow region of small pressures nearby the melting curve, where the sign of the coefficient \( \alpha \) is negative [7].

With increasing pressure, the number density of vacancies in a solid increases, according to the relation

\[ n = (n_0 T_0/T) \exp \left(- (E_0 - \alpha P/n_0) / T \right), \]  

(6)

and, finally, the vacancies can condense, forming their own sub-lattice. Such is the explanation of the appearance of composite incommensurate structures in metals and some other elemental solids under high pressure [1-4]. For example, the structure of phase IV of barium is composed of a tetragonal ‘host’, with ‘guest’ chains in channels along the \( c \) axis of the host. These chains form two different structures, one well crystallized and the other highly disordered. The guest structures are incommensurate with the host [1]. Rb- IV has an incommensurate composite structure, comprising a tetragonal host framework and a simple body-centered tetragonal guest, the ratio of the \( c \)-axis lattice parameters being strongly pressure dependent [2].

Further increase of the number density of vacancies in a solid with increasing pressure leads to the melting of the solid under sufficiently high pressure (and fixed temperature). Such effect has been observed in sodium [5]. In general, such behavior is universal for solids, though the corresponding melting pressure is typically much larger than those for sodium.
The melting pressure $P_m$ at low temperatures can be estimated from the relation

$$P_m \approx n_0 T_m, \quad (7)$$

where $T_m$ is the melting temperature at ambient pressure. The temperature dependence of the melting pressure (or, equivalently, the pressure dependence of the melting temperature in the region of high pressures) is considered below.

At the melting pressure $P = P_m$, the energy of the vacancy formation (5) is small and can be put to be approximately equal to zero,

$$E_v = E_0 - \alpha P/n_0 \approx 0. \quad (8)$$

Taking into account the relation (7), from the equation (8) we obtain

$$\alpha \approx E_0 n_0 / P_m \approx E_0 / T_m. \quad (9)$$

There is an empirical relation between the activation energy of self-diffusion and the melting temperature of a solid [7]. Due to the atomic relaxation in a crystalline solid, the migration barrier for a vacancy is low, so that the activation energy of self-diffusion is approximately equal to the energy of the vacancy formation. For the most of metals, this relation has a form

$$E_0 \approx 18 T_m, \quad (10)$$

and from the equation (9) we find $\alpha \approx 18$. Thus, for the most of metals, the formula

$$n \approx (n_0 T_0 / T) \exp \left( - (E_0 - 18P/n_0) / T \right) \quad (11)$$

is valid. For anomalous body centered cubic metals ($Ti - \beta$, $Zr - \beta$, $U - \gamma$, and others), at low temperatures the relation $E_0 \approx 12T_m$ is valid, so in this case $\alpha \approx 12$.

The low values of the activation energy of self-diffusion in anomalous bcc metals seem to be produced by the stresses associated with the phase transition from a low-temperature dense phase to a high-temperature bcc phase [7]. The effect has a local character in the temperature-pressure plane, so in the region of high pressures the value of the coefficient alpha, $\alpha \approx 18$, is universal for crystalline solids.
Replacing in the relation (6) the pressure $P$ by the absolute value of the stress or tension $\sigma = F/S$, applied to a solid, where $F$ is the applied force and $S$ is the cross-section area of the solid in the plane perpendicular to the direction of the applied force, we can estimate the mean number density of vacancies in the solid under the stress or tension:

$$\langle n \rangle \cong (n_0 T_0 / T) \exp \left( - \left( E_0 - \alpha \sigma / n_0 \right) / T \right). \quad (12)$$

Here, for the most of metals the value of the constant $\alpha$ is $\alpha \approx 18$, and for the anomalous $bcc$ metals this constant is $\alpha \approx 12$.

The dissolution of the vacancy gas in a solid under the stress or tension is responsible for the low values of the elastic limit and the tensile strength of solids as compared with theoretical estimations not taking into account this process [8].

As can be inferred from the relation (7) as compared with the experimental data, there are some systematic errors in the calibration of high pressure. This conclusion is supported by those fact that the ratio of ‘measured’ pressure and the value of pressure expected from the relation (7) has the same order of magnitude as the ratio of theoretical (calculated) and real tensile strengths of solids [8].

The melting pressure at low temperatures has an order of magnitude of the tensile strength of a solid, $P_m \cong \sigma_s$, so from equation (7) we find

$$n_0 \cong \sigma_s / T_m. \quad (13)$$

This relation gives another estimation of the constant $n_0$. For iron $T_m = 1800K = 1.88 \times 10^{-13} erg$, $\sigma_s = 3 \times 10^9 dyn/cm^2$, and relation (13) gives $n_0 \cong 1.2 \times 10^{22} cm^{-3}$. For silver $T_m = 1230K = 1.7 \times 10^{-13} erg$, $\sigma_s = 1.8 \times 10^9 dyn/cm^2$, and equation (13) gives $n_0 \cong 1.1 \times 10^{22} cm^{-3}$.

Since the pressure acts as an energy factor similar to the temperature, it normally causes the decrease of the critical temperature of phase transitions in solids. For example, for single-metal superconductors the critical temperature of the phase transition is found to decrease under pressure [9]. Ferromagnets also normally show the decrease of the Curie temperature with pressure [10]. Similar is the behavior of the Curie temperature of ferroelectrics [11].

Superconducting phase transitions in metals and cuprate oxides under high pressure [9,12,13] are described by the relation
\[ T_c + kP/n_0 = \text{const}, \]  

\( (14) \)

where \( T_c \) is the critical temperature of the transition and \( k \) is a constant dependent on the chemical composition. The relation \( (14) \) is also valid for weak itinerant ferromagnets [10] and ferroelectrics [11]. The equation \( (14) \) describes also the melting of a solid under sufficiently high pressure, the constant \( k \) in this case being \( k \approx 1 \) [14].

To summarize, the dissolution of the vacancy gas in solids under pressure determines both the structural transitions and the melting of a solid in the high-pressure region. The dissolution of vacancies in solids under the stress or tension leads to the low values of the elastic limit and the tensile (or compression) strength of solids. The treating of the pressure as an energy factor similar to the temperature can explain the linear dependence of the critical temperature of a phase transition on the pressure observed in superconductors, ferromagnets, and ferroelectrics.

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