

Thermodynamics and microstructure of vacancies in rare gas crystals at high temperature

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Received September 7, 2006

A self-consistent statistical method is used to calculate the Gibbs free energy of vacancy formation in heavy rare gas crystals at high temperature. It is shown that the vacancy formation free energy rapidly falls in the vicinity of the melting point of the crystal. Such behavior is attributed to approaching the anharmonic instability point of vibrational subsystem of the solid.

PACS: 61.72.Bb Theories and models of crystal defects;
61.72.Ji Point defects (vacancies, interstitials, color centers, etc.) and defect clusters;
64.70.Dv Solid-liquid transitions.

Keywords: vacancy formation, rare gas crystals.

1. Introduction

Point defects in rare gas crystals (RGC) have been extensively studied both theoretically and experimentally for about fifty years. Indeed, the RGC remain popular research objects of the condensed matter physics because the many-body interactions in these systems may be effectively described by a sum of two-body interactions, approximated by various empirical potentials [1] (though explanation of some fine effects requires many-body interactions to be invoked [2]).

Since there is a great bulk of experimental data accumulated on various physical properties of the RGC, they are ideal systems for testing various microscopic theories. For instance, it appeared that the classical lattice dynamics failed in description of strongly anharmonic atomic motion in the RGC at high temperature [3]. Realization of this fact became a challenge that stimulated attempts to work out some methods for adequate self-consistent description of strongly anharmonic solids. At present, existing theoretical models [4–7] predict well enough thermal and elastic properties of the bulk RGC in a wide range of temperature and pressure, in agreement with the experimental data available.

However, as for properties of point defects in the RGC, the picture is not so fair. Since the RGC form closed-packed structure (fcc), vacancies represent the predominant thermal defect in these solids. To determine directly the equilibrium concentration c_v of vacancies in the RGC, the most accurate

and reliable experimental method is simultaneous measurement of length and x-ray lattice parameter of a specimen [8,9]. Some authors extracted c_v data from comparison of measured bulk properties of the crystal (length, density, thermal expansion coefficient) [10–14] with corresponding x-ray data [8,15–17]. Even measured values of the vacancy concentration show remarkable divergency. For instance, reported values of c_v near the triple point are for Ar: $< 10^{-3}$ [12], $< 2 \cdot 10^{-4}$ [9], $< 3 \cdot 10^{-3}$ [15], $1.0 \cdot 10^{-2}$ [14]; for Kr: $7.4 \cdot 10^{-3}$ [14], $3.2 \cdot 10^{-3}$ [8], $2.9 \cdot 10^{-3}$ [13]; for Xe: 10^{-2} [16], $1.2 \cdot 10^{-1}$ [14].

Thermodynamical parameters of vacancies, such formation enthalpy, entropy, volume, etc., are extracted from the observed data by indirect methods. Vice versa, microscopic calculations deal with direct evaluation of energetic parameters of the vacancy. At present, there is a variety of theoretical predictions of vacancy formation parameters made by different authors via various methods, including Monte Carlo calculations [18,19] (see, e.g., Refs. 9, 20, 21 where results of various calculations are compared). Numerous calculations of vacancy properties have been made, taking such factors into account as static lattice relaxation, change of vibrational frequencies, lattice anharmonicity, quantum and many-body corrections [20]. In spite of some discrepancy between the calculated values of the vacancy parameters reported by different authors, we may, in principle, assert that there is qualitative agreement between calculated and observed values. For example, the computed values of

the vacancy concentration in Ar near the triple point are 10^{-4} – 10^{-3} in order [21–24]. It is generally agreed that the Gibbs free energy of vacancy formation decreases nearly linearly with temperature, though the idea that it can decrease rapidly near the triple point was suggested to explain anomalous behavior of isohoric specific heat of argon [25].

The aim of the present study is calculation of vacancy parameters in the RGC at high temperature by means of the self-consistent statistical method for determination of thermodynamical properties of anharmonic solids developed in Ref. 6. The basics of this method are briefly outlined in Sec. 2 in relation to the subject of this work. In Sec. 3 we substantiate the high-temperature approximation to the self-consistent statistical method. Then in Sec. 4 we set out the procedure of calculation of the Gibbs free energy of vacancy formation in the RGC at high temperature. The results of our studies for Ar are presented in Sec. 5, and in Sec. 6 a brief conclusion is given.

2. Self-consistent statistical method

To describe thermal properties of equilibrium vacancies in a crystal, we should first write down the Gibbs free energy of vacancy formation as a function of temperature T and external pressure P ,

$$g(T, P) = G_1(T, P) - G_0(T, P), \quad (1)$$

where G_0 and G_1 are, respectively, the Gibbs free energies of a hypothetical perfect crystal and a crystal containing one vacancy at a fixed lattice site. If the vacancies are assumed to be noninteracting, their equilibrium concentration is given by

$$c(T, P) = \exp [-g(T, P) / k_B T]. \quad (2)$$

Microscopic calculation of $g(T, P)$ requires both evaluation of the Gibbs free energy of a perfect crystal at given temperature and pressure and proper description of the system response on creation of a defect. Since the number of vacancies becomes appreciable near the melting point only, it is worthwhile to restrict the consideration of their properties with the high-temperature range, incorporating properly effects of anharmonicity of atomic vibrations. For this purpose, we follow a recently proposed self-consistent statistical method for calculation of thermodynamical properties of solids [6]. According to this approach, the Gibbs free energy of a simple perfect crystal consisting of N atoms of mass m is written in the form of the Gibbs–Bogoliubov functional corrected for the cubic anharmonicity,

$$G_0 = F_H + \langle U - U_H \rangle + F_3 + PV, \quad (3)$$

where F_H and $\langle U_H \rangle$ are, respectively, the Helmholtz free energy and the average potential energy of a reference harmonic crystal, F_3 is a correction for the cubic

anharmonicity of atomic vibrations evaluated within the second-order perturbation theory, and

$$U = \frac{1}{2} \sum_{i,j=1}^N u(r_{ij}) \quad (4)$$

is the potential energy of interatomic interaction which is assumed to be central and pairwise and is approximated by an empirical potential $u(r)$. As in Refs. 26, 27, we employ here a hybrid potential of interatomic interaction. The interaction of nearest neighbors is described by the exponential Morse potential,

$$u(r) = A [e^{2\alpha(r-R_0)} - 2e^{-\alpha(r-R_0)}] \quad (5)$$

which is especially convenient for the possibility of analytical calculations of average values. However, it does not provide the proper long-range asymptotics of the van der Waals attraction of atoms in the RGC ($\sim -r^{-6}$), so we use the attractive part of the Lennard–Jones potential $u(r) = -4\epsilon(\sigma/r)^6$ to approximate interactions of atoms that are not nearest neighbors of each other.

The parameters A , α , and R_0 were determined in Ref. 27 so that the present model reproduced the observed values of sublimation energy, interatomic distance, and bulk modulus of the RGC at $T = 0$. The parameters ϵ and σ were obtained in a similar way within the model using the Lennard–Jones (12–6) potential only [6]. The values of the parameters A , R_0 , α , ϵ and σ for the RGC are listed in Table 1.

Table 1. Parameters of the Morse and Lennard–Jones potentials and the de Boer parameters Λ for the heavy RGC

RGC	$\alpha, \text{\AA}^{-1}$	A, K	$R_0, \text{\AA}$	$\sigma, \text{\AA}$	ϵ, K	Λ
Ar	1.63	117	3.83	3.37	132.52	0.165
Kr	1.52	172	4.09	3.61	182.85	0.088
Xe	1.38	226	4.46	3.92	257.34	0.055

The average potential energy $\langle U \rangle$ in (3) is calculated over correlated Gaussian distribution function of atomic coordinates. The parameters of this distribution are determined by the phonon spectrum of the crystal parametrized by a single dimensionless parameter c of effective quasi-elastic bond of neighboring atoms [6]. For the Morse potential, the average potential energy of interaction of two neighboring atoms can be expressed analytically as

$$\langle u \rangle = A [e^{-2b+q/\gamma\alpha^2} - 2e^{-b+q/4\gamma\alpha^2}], \quad (6)$$

where $b = \alpha(R - R_0)$ is a reduced lattice expansion, R is the nearest-neighbor distance, γ is the inverse square of a width of the distribution, and q is a dimensionless factor

representing a contribution of the correlations to the energy of interatomic interactions ($q=2$ in the absence of correlation).

The explicit formulae for F_H, U_H, F_3 , and for the distribution width function of atomic displacements are given in Ref. 6. Minimization of the functional (3) with respect to the parameters c and b allows us to compute thermodynamical properties of the perfect crystal at arbitrary T and P . A limit temperature T_c , above which the minimum of G_0 with respect to c does not exist anymore, defines the point of the instability of the solid due to the strong vibrational anharmonicity. For the perfect heavy RGC, $T_c \approx 0.716 A$ at $P=0$, i.e., T_c is slightly higher than the observed melting point.

3. The high-temperature limit

Now let us write down the Gibbs free energy of vacancy formation,

$$g(T, P) = -\frac{1}{2} \sum_{i>0} \langle u(r_{0i}) \rangle + \Delta F_R + P\nu, \quad (7)$$

where the first term describes a change of the crystal energy due to creation of a vacancy without any regard for atomic relaxation around it, ν is a vacancy volume (assumed to be equal to the atomic volume, $R^3/\sqrt{2}$ in the fcc lattice), and ΔF_R is a change of the crystal free energy due to medium relaxation around the vacancy, including lattice distortion and changes of atomic vibrational frequencies.

To evaluate the first term in (7), we need the parameters of the perfect crystal only, so it may be considered as a first-order approximation to the true $g(T, P)$. However, the atomic relaxation may contribute substantially to (7), especially in the vicinity of the point of the high-temperature instability of the crystalline state. To estimate ΔF_R , we should allow for a change of the vibrational spectrum due to the vacancy formation, which is, generally, rather complicated.

Since we are concerned with the vacancy properties at high temperatures, it seems reasonable to benefit from the one-particle approximation which is known to provide a good description of vibrational and thermodynamical properties of solids in this temperature range [20]. It was shown in Ref. 6 that a contribution of the interatomic correlations to the average potential energy of the crystal can be discarded at high temperature ($q \rightarrow 2$ in (6)), so that we can use a one-particle distribution function of atomic displacements, represented by a Gaussian function

$$f(\mathbf{q}_i) = \left(\frac{\gamma}{\pi} \right)^{3/2} \exp(-\gamma q_i^2), \quad (8)$$

with \mathbf{q}_i being a displacement of the atom from its site. The inverse square of the distribution γ can be presented as a power series [6]

$$\gamma(c, \tau) = \frac{c^2 \alpha^2}{\tau} \sum_{l=0}^{\infty} n_{2l} (-1)^l \left(\frac{c\Lambda}{\tau} \right)^{2l}. \quad (9)$$

Here c is the parameter of effective quasi-elastic bond of neighboring atoms, $\tau = k_B T/A$ is reduced temperature, and

$$\Lambda = \frac{\hbar \alpha}{\sqrt{mk_B A}} \quad (10)$$

is the de Boer parameter for the Morse potential, m is atomic mass. The condition $c\Lambda/\tau \ll 1$ defines the range of applicability of the high-temperature approximation. The coefficients n_{2l} in (9) are determined by integration over the phonon spectrum of the crystal, and in the case of the fcc lattice the first four of them are $n_0 = 2$, $n_2 = 5/6$, $n_4 = 0.475$ and $n_6 = 0.296$ [6].

In the high-temperature approximation the average potential energy (6) of interaction of neighboring atoms takes on the form

$$u^* = \frac{\langle u \rangle}{A} = e^{-2b+2/\gamma^*} - 2e^{-b+1/2\gamma^*} \quad (11)$$

with $\gamma^* = \gamma/\alpha^2$, while the long-range van der Waals interaction of other pairs of atoms is taken into account without thermal averaging. Hereafter we will preferably represent energy in units of A .

The other contributions to $G_0(T, P)$ in the high-temperature limit appear as [6]

$$\varphi_s = \frac{F_H - \langle U_H \rangle}{A} \approx \tau \left[\frac{1}{3} + \frac{1}{48} \left(\frac{c\Lambda}{\tau} \right)^4 \right] + 3 \tau \log \left(\frac{c\Lambda}{\tau} \right), \quad (12)$$

$$\varphi_3 = \frac{F_3}{A} \approx -\frac{a_3 \tau^2}{c^6} \left(e^{-2b+2/\gamma^*} - \frac{1}{4} e^{-b+1/2\gamma^*} \right)^2, \quad (13)$$

where the dimensionless coefficient $a_3 = 2.2$ describing effective cubic anharmonicity contribution is chosen so that the calculated instability temperature at $P=0$ lies close to the triple point. Thus, the Gibbs free energy of the perfect crystal at high temperature is written as

$$\frac{G_0^{HT}}{AN} = \frac{z_1}{2} u^* - \kappa \frac{\varepsilon}{A} \left(\frac{\sigma}{R} \right)^6 + \varphi_s + \varphi_3 + \frac{p(\alpha R)^3}{\sqrt{2}}, \quad (14)$$

where $z_1 = 12$ is the coordination number, $\kappa = 4.91$ for the fcc lattice [28], and $p = P/(\alpha^3 A)$ is reduced pressure.

A test of this model shows that it provides an excellent description of thermodynamical properties of essentially classical Xe crystal ($\Lambda = 0.055$), even at $\tau > 0.15$. (Note that the instability point $\tau_c \approx 0.72$ for all the heavy RGC.) Moreover, the classical approximation $\Lambda = 0$ appears in that case satisfactory, too. On the other hand, for Ar ($\Lambda = 0.165$) the high-temperature approximation becomes valid only at $\tau > 0.45$.

4. Vacancy

The high-temperature approximation to the self-consistent statistical method gives us a tool for description of thermodynamical properties of the vacancies in the heavy RGC. The following assumptions will be made in consideration of the atomic relaxation around the vacancy.

1. The vacancy is assumed to be at the origin of the crystal. The relaxation of the atomic distribution in four coordination spheres of the vacancy is taken into account. The parameters of the other atoms are assumed to be unchanged in comparison with those of the perfect crystal.

2. An equilibrium position of each of the relaxing atoms is shifted radially by a distance ΔR_n , where n is the number of the coordination sphere. We assume $\Delta R_n > 0$ for outward relaxation.

3. The distribution function of an atom of the vacancy's n th coordination sphere is axially symmetrical and is written as

$$f^{(n)}(x, y, z) = C_n \exp[-\gamma(c_{n1}, \tau)x^2 - \gamma(c_{n2}, \tau)(y^2 + z^2)], \quad (15)$$

where c_{n1} and c_{n2} are variational parameters characterizing longitudinal and transverse widths of distribution, respectively, and the x axis is chosen so that it passes through the site of the atom and the vacancy. The functional form of the $\gamma(c, \tau)$ is assumed to be given by Eq. (9).

4. Only pairs of neighboring atoms are assumed to contribute into the change of the potential energy of interatomic interaction in the vacancy's surrounding.

Changes of the average vibrational amplitudes of atoms around the vacancy affect the potential energy of interatomic interaction (through the parameter γ), the entropy term φ_s , and the cubic correction φ_3 . A change of the entropy term is evident,

$$\Delta\varphi_s = \sum_{n=1}^4 \frac{z_n}{3} [\varphi_s(c_{n1}) + 2\varphi_s(c_{n2}) - 3\varphi_s(c_0)], \quad (16)$$

where z_n is the number of atoms in the n th coordination sphere of the vacancy, $\varphi_s(c)$ is given by (12), and c_0 is the quasi-elastic bond parameter for the perfect crystal.

A change of the average potential energy of interaction between two neighboring atoms belonging to the n th and m th coordination spheres of the vacancy is determined by angles and sides of a triangle formed by the sites of these atoms and the vacancy,

$$\Delta u_{nm}^* = e^{-2b_{nm} + \lambda_{nm}} - 2e^{-b_{nm} + \lambda_{nm}/4} - u^*, \quad (17)$$

where $b_{nm} = \alpha(R_{nm} - R_0)$,

$$R_{nm} \approx R \left[1 + \Delta_n \left(\sqrt{n} + \frac{1-m}{\sqrt{n}} \right) + \Delta_m \left(\sqrt{m} + \frac{1-n}{\sqrt{m}} \right) \right]^{1/2}$$

is a changed distance between the atoms, $\Delta_n = \Delta R_n / R$ is a reduced shift of an atom from the vacancy's n th coordination sphere,

$$\lambda_{nm} = \frac{\cos^2 \theta_{nm}}{\gamma^*(c_{n1})} + \frac{\sin^2 \theta_{nm}}{\gamma^*(c_{n2})} + \frac{\cos^2 \theta_{mn}}{\gamma^*(c_{m1})} + \frac{\sin^2 \theta_{mn}}{\gamma^*(c_{m2})},$$

and $\cos^2 \theta_{nm} = (1 + n - m)^2 / 4n$. Then the reduced potential energy contribution to the free energy of the medium relaxation is given by

$$\Delta U^* = \sum_{n=1}^4 z_n \left[\frac{z_{nn} \Delta u_{nn}^*}{2} + \sum_{m>n} z_{nm} \Delta u_{nm}^* \right], \quad (18)$$

where z_{nm} is a number of atoms belonging to the m th coordination sphere of the vacancy that are the nearest neighbors of an atom from the n th sphere.

Finally, we have to allow for a cubic anharmonicity contribution to the vacancy formation free energy. Generalizing Eq. (13) on the situation when atomic vibrational distributions are not isotropic, we write

$$\Delta\varphi_3 = \sum_{n=1}^4 z_n [-\varphi_3(c_0, \tau) + \sum_{m=1}^4 z_{nm} \varphi_3^{nm}], \quad (19)$$

where

$$\varphi_3^{nm} = -\frac{a_3 \tau^2}{27} \left[e^{-2b_{nm} + \lambda_{nm}} - \frac{1}{4} e^{-b_{nm} + \lambda_{nm}/4} \right]^2 \times \sum_{ijk=1}^3 (c_{ni} c_{nj} c_{nk})^{-2}, \quad (20)$$

with $c_{n3} \equiv c_{n2}$.

We should keep in mind that Eq. (13) was derived in the high-temperature limit from a general expression for the cubic anharmonic contribution to the vibrational part of the free energy of a perfect crystal [29], with the factor a_3 determined by the phonon spectrum of the perfect crystal. Since presence of a vacancy distorts substantially the vibrational spectrum of the crystal, we can use Eq. (19) only for a qualitative estimation of the cubic contribution to the free energy of an imperfect crystal.

Thus, within the present model, the Gibbs free energy of vacancy formation in the RGC is a function of twelve variational parameters c_{n1} and Δ_n and is written as

$$\frac{g(\tau, p)}{A} = -\frac{z_1}{2} u^* + \kappa \frac{\varepsilon}{A} \left(\frac{\sigma}{R} \right)^6 + \frac{p(\alpha R)^3}{\sqrt{2}} + \Delta U^* + \Delta\varphi_s + \Delta\varphi_3. \quad (21)$$

5. Results and discussion

We calculated the equilibrium value of the Gibbs free energy of vacancy formation for Ar and Xe, minimizing $g(\tau, p)$ with respect to a set of variational parameters. It turned out that inclusion of a contribution of the nearest neighbors of the vacancy to the cubic anharmonic correction (19) results in disappearance of the minimum of g with respect to c_{11} and c_{12} at temperature slightly below the bulk instability point τ_c . To override this artefact, we had to discard the cubic anharmonic contribution of the first coordination sphere of the vacancy. We suppose that for the vacancy's nearest neighbors, located in essentially nonspherical potential wells, the cubic correction to $g(\tau, p)$ is of more sophisticated form than that given by (19) and (20). Thus, the value of the vacancy formation free energy calculated with this contribution discarded represents the upper limit of $g(\tau, p)$. However, our estimation showed that $g(\tau, p)$ is only slightly sensitive to inclusion of the anharmonic contribution of the first coordination sphere, though this may be not a case in the vicinity of the instability point.

In Fig. 1 we plotted the temperature dependence of the vacancy formation free energy g at zero pressure calculated for Ar and Xe (solid lines). In the same plot we show $g(T)$ computed for a quasi-harmonic crystal, i.e., with $a_3 = 0$ (dash lines), and for an anharmonic crystal, but without the cubic contribution (19) included to the vacancy formation free energy (dot lines). Near the melting point the calculated vacancy concentration in both crystals is about $1.6 \cdot 10^{-4}$. This value agrees with the results of some experimental [9] and theoretical [18,22,23] studies, though it is less by the order of magnitude than that of others [14,15,21,23]. To compare our results for the vacancy parameters in Ar with others available in the literature, we collected some experimental and calculated data in Table 2.

The central result of this study is a drastic reduction of the vacancy formation free energy near the melting temperature due to approaching the point of the solid state instability.

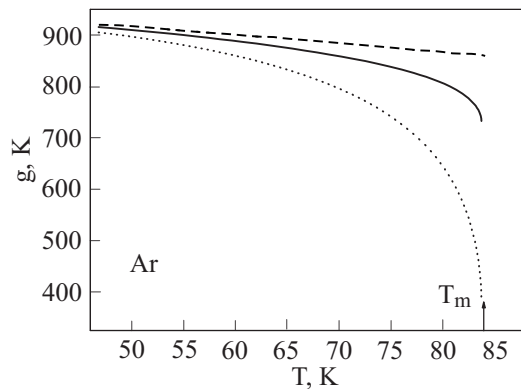


Table 2. Vacancy parameters for Ar near the triple point: formation enthalpy, entropy, Gibbs free energy, and concentration.

Ref.	h, K	s, k_B	g, K	$10^4 c_v$	Method
[9]	–	–	–	< 2.5	Simultaneous measurement of bulk and lattice expansion
[15]	–	–	–	30	Measurement of x-ray lattice parameters along the melting line; comparison with bulk data
[14]	943.6	6.72	392.6	108	Measurement of coefficient of thermal expansion; comparison with x-ray data
[22]	957.5	4	–	5.5	Two-body quasi-harmonic model
[18]	–	–	–	4	Monte Carlo two-body simulation
[24]	857	2	689.4	3.5	Self-consistent Einstein model
[23]	805.4	–	–	18.6	Correlative method of the unsymmetrized self-consistent field
[21]	802.3	–	529.4	18.1	Statistical theory of mixtures
This work	1225	5.9	733	1.6	Self-consistent statistical method

This is also indicative of sharp increase of the vacancy formation entropy $s = -(\partial g / \partial T)_P$ from about $2 k_B$ at $\tau \sim 0.45$ to $5.6 k_B$ at τ_c . At the same time, the vacancy formation enthalpy $h = g + Ts$ also increases near the instability point, from $h \approx 1000$ to 1216 K in the considered temperature range. The idea that the vacancy formation enthalpy can rapidly increase near the triple point of a crystal was suggested by Crawford et al. [25] for explanation of anomalous high-temperature behavior of the isohoric specific heat of Ar. They also presumed that such behavior of vacancy parameters may be attributed to the vicinity of the solid state instability point.

In Fig. 2 we show spatial distribution of the equilibrium values of longitudinal ($l = 1$) and transverse ($l = 2$) parameters

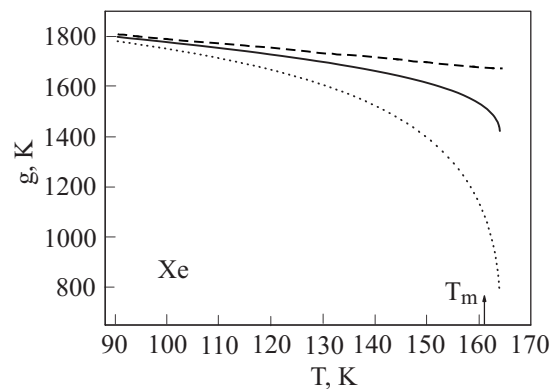


Fig. 1. Temperature dependence of the Gibbs free energy of vacancy formation in Ar and Xe at zero pressure calculated: for a quasi-harmonic crystal (dash lines); for an anharmonic crystal (solid lines); for an anharmonic crystal without taking into account the cubic correction to the vacancy formation free energy (dot lines).

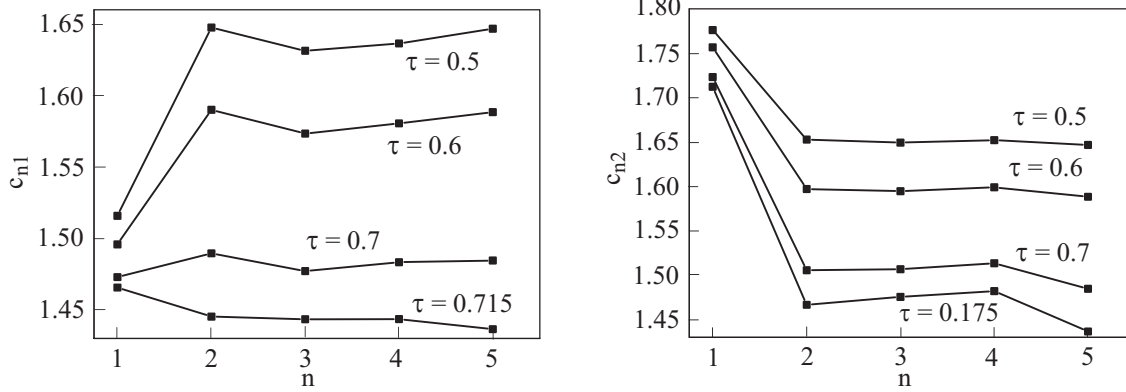


Fig. 2. A profile of the longitudinal (c_{n1}) and transverse parameters (c_{n2}) of the distribution of atomic displacements around the vacancy in Ar at different temperatures, n is a coordination sphere number, $n = 5$ corresponds to the bulk value of c .

c_{n1} in Ar at different temperatures. Note that c_{n1} and c_{n2} determine the average amplitudes of radial and tangential vibrations of atoms around the vacancy, respectively (the mean-square average displacement $\langle q^2 \rangle \sim c^{-2}$ [6]). As one may expect, the presence of a vacancy affects mostly the distributions of displacements of its nearest neighbors, which appear to be substantially elongated towards the vacancy. The distributions of the other atoms around the vacancy remain almost spherical. Unfortunately, our model does not reproduce properly the behavior of parameters c_{11} and c_{12} near the instability point, since we ignored the contribution of the vacancy's first coordination sphere to the $\Delta\phi_3$. One should expect that these parameters decrease more steeply as temperature approaches T_c , thus providing additional reduction of the free energy of vacancy formation.

Figure 3 represents spatial distribution of relative shifts $\Delta_n = \Delta R_n / R$ of the equilibrium positions of Ar atoms around the vacancy at different temperatures. The shifts of atoms are negative within the considered temperature range, i.e., the atomic relaxation is inward. A contribution of the spatial medium relaxation to the vacancy formation energy varies from 1.6% at $\tau = 0.4$ to 4% near τ_c in comparison with the value of g calculated taking into account changes of

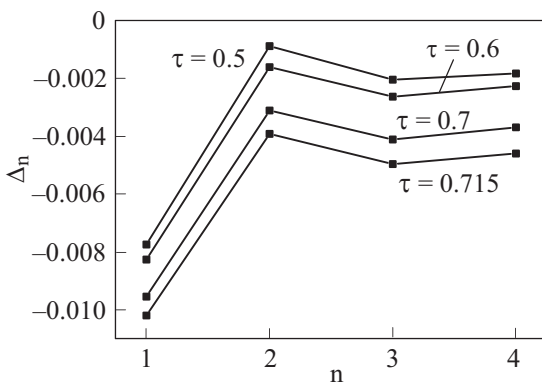


Fig. 3. Distribution of the relative shifts of the equilibrium positions of Ar atoms belonging to the four coordination spheres of the vacancy at different temperatures.

the amplitudes of atomic vibrations only. These results are quite consistent with that of Glyde [20,30].

We also considered influence of external pressure on vacancy formation in the RGC near the melting line. Particularly, we checked the assumption that the vacancy concentration is constant along the melting line [31]. We successfully tested the present high-temperature approximation to the self-consistent statistical model by calculation of the equation of state for perfect Ar crystal at 293 K up to 80 GPa. The agreement with observed data is quite good within the considered pressure range.

At low pressures (< 8 kbar) the calculated temperatures of the solid state instability are only slightly higher than the observed melting point, but at higher pressures the instability line lies much above the melting line. Therefore, the condition $c_v = \text{const}$ along the melting line is valid at least at low pressures where the curves $T_c(P)$ and $T_M(P)$ almost coincide.

Due to the assumptions we adopted in the present study, we consider our results for the vacancy formation free energy as an upper limit for the true $g(T, P)$. First, to improve the present model, we should take proper account of the cubic anharmonic contribution of the nearest neighbors of the vacancy. Second, we used a rather simple model to describe the long-range interaction of atoms which can also contribute to the potential energy of the medium relaxation. It is also worthwhile to seek for the equilibrium value of c_v simultaneously with that of the bulk variational parameters c and b , as it was made in Ref. 24. Moreover, an analysis of this problem suggests that the calculated thermodynamical properties of the vacancies are much more sensitive to the input parameters and assumptions than the bulk crystal thermodynamics. For example, the long-range many-body effects are known to decrease the vacancy formation enthalpy by 6% for Ar and Kr at $T = 0$ and by 8% for Xe [32]. Another point is that perturbation of the phonon spectrum due to creation of vacancies is, indeed, more complicated than that described by the one-particle approximation. These and other effects may be of crucial importance in the

premelting temperature range, so that the role vacancies play in the melting transition cannot be discarded.

6. Conclusion

To conclude, let us discuss the role the vibrational anharmonicity plays in formation of structure defects in a crystal. An emphasis will be placed on the cubic vibrational anharmonicity, which is of crucial importance for the evolution of instability of the phonon subsystem of the crystal. To get an insight into the nature of such instability, we should keep in mind that the odd order anharmonicity corresponds to effective attraction between phonons. In a crystal with the cubic anharmonicity, the phonon subsystem can be considered as a nonideal gas of attracting particles, with the number of particles being an internal parameter of the system. On the contrary, the even order anharmonicity corresponds to effective repulsion of phonons and, as known [33], is related to another type of instability at temperatures much higher than the melting point of the solid.

At high temperature, the cubic anharmonicity is responsible for the nonlinear reduction of the quasi-elastic bond parameter $c_0(\tau)$ with temperature, especially in the vicinity of the critical temperature τ_c . Such behavior of $c_0(\tau)$ manifests itself in increasing of the widths of atomic distributions and, as a result, in a nonlinear rise of the average potential energy of the interatomic interaction. Since creation of structural defects in the crystal, such as vacancies, is accompanied by rupture of a part of interatomic bonds, a dramatic drop of the binding energy near the instability point paves the way for the structural disordering of the medium, i.e., for the melting transition. In our previous works [6,26,27,34] we show that the premelting effects in the RGC (nonlinear rise of isobaric specific heat, coefficient of thermal expansion etc.) are associated with the evolution of the solid state instability. Up to concentrations $c_v \sim 10^{-2}$, vacancies have only little influence on the crystal's thermodynamical properties. However, in the direct vicinity of the instability temperature, the vacancy contribution to the system thermodynamics is comparable with the bulk one [34]. Finally, note that steep temperature dependence of the free energy of the vacancy formation near τ_c can be responsible for large divergency of observed values of the vacancy concentration in the RGC [8,9,12–16].

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