

## Role of anharmonicity of atomic vibrations in formation of vacancies in rare-gas crystals

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We use a self-consistent statistical method to study formation of vacancies in rare-gas crystals at high temperature. The vacancy formation energy is calculated by minimization of the relaxation energy of the vacancy surrounding with respect to distribution parameters of atomic displacements for four coordination spheres of the vacancy. An emphasis is placed on the analysis of the role the vibrational anharmonicity plays in formation of defects in a crystal at high temperature. It is shown that the vacancy formation energy rapidly falls as temperature approaches the melting point of the crystal. Assuming that the crystal melts as temperature reaches the region of instability of the solid state, we compute the melting curve of Ar.

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In the present study we consider the formation of vacancies in heavy rare-gas crystals (RGCs) in the high-temperature range, where the anharmonicity of atomic vibrations contributes substantially to the thermodynamic properties of solids. The data on the value of the concentration of vacancies in solids, available in the literature, are rather contradictory, especially, for high temperatures near the melting point (see, e.g., Refs. 1–4). Examining the mechanism of formation of vacancies is important to understand the nature of melting of crystals. It is known that normal melting is accompanied by rupture of a part of interatomic bonds and by reduction of the coordination number of atoms, while the average interatomic distance remains practically unchanged. There is still a great deal to learn about the physical mechanism responsible for the breakdown of ordering of atoms in the crystal as temperature increases.

The aim of this study is to elucidate the contribution of the vibrational anharmonicity to the relaxation of medium around a vacant site. As we demonstrate below, the anharmonicity of atomic vibrations leads, in comparison with a quasiharmonic crystal, to the accumulation of an excess of the potential energy of interatomic interactions. The excessive potential energy is released, when the medium relaxes around a vacant site, thus reducing the formation energy of the vacancy. Such energy lowering is especially pronounced in the vicinity of the instability point of the crystalline state associated with the vibrational anharmonicity.<sup>5–7</sup> As a result, one may expect that a phase containing a large number of defects becomes thermodynamically favorable.

To describe the relaxation of the medium around a vacant lattice site and to calculate the vacancy formation energy, we employ the self-consistent statistical method of calculation of thermodynamical properties of solids proposed in Ref. 5. The method consists in derivation of the binary distribution function of atomic displacements and a variational procedure of calculation of effective parameters of the quasielastic bond of atoms. Our approach has much in common with the well-known self-consistent phonon theory,<sup>8–10</sup> however, the variational procedure is simpler in calculations and even allows one to obtain an analytical representation of thermodynamic properties of the crystal

for certain temperature and pressure ranges. This approach was successfully applied to compute thermal properties and equation of state of the RGC, resulting in a good agreement between the calculated and the experimental data over wide ranges of temperature and pressure.<sup>5,6</sup> It was demonstrated<sup>5</sup> that, in addition to the quantum and the thermal contributions to smearing of the range of localization of atoms, there is an additional correlative contribution which, along with above factors, enhances the repulsion between neighboring atoms of the crystal. The analysis of the theoretical model<sup>5</sup> revealed that the contribution to the potential energy of interatomic interaction due to the correlations of atomic motion is almost completely compensated at high temperature by the enhancement of interatomic repulsion due to the correlative smearing of the range of localization of atoms. In other words, in the framework of the present statistical model, the correlations of atomic displacements do not contribute to the crystal potential energy at high temperature. So, the motion of atoms of the crystal can be considered uncorrelated. In this situation, to calculate the average potential energy, one may represent the distribution function of the crystal as a product of uncorrelated one-particle functions. For example, if the pairwise interaction of neighboring atoms of a RGC is approximated by the Morse potential

$$u(r) = A[e^{-2\alpha(r-R_0)} - 2e^{-\alpha(r-R_0)}] \quad (1)$$

with the three parameters  $A$ ,  $R_0$ , and  $\alpha$ , the distribution function of the atom  $n$  of a perfect crystal can be written in the Gaussian form

$$f(\mathbf{q}_n) = C \exp\left(-\frac{2\alpha^2 c^2 q_n^2}{\tau}\right), \quad (2)$$

where  $\mathbf{q}_n$  is the displacement of the atom from its site,  $\tau = T/A$  is the reduced temperature, and  $c$  is a dimensionless effective parameter of the quasielastic bond of neighboring atoms. Then Gibbs thermodynamic potential  $\Phi_0$  of the crystal is expressed as<sup>5,6</sup>

$$\begin{aligned}
g(\tau, P, c, b) = & \frac{\Phi_0}{AN} = \left( \frac{\tau}{3} + 3\tau \ln \frac{c\Lambda}{\tau} \right) + \frac{z}{2} [e^{-2b+\tau/c^2} \\
& - 2e^{-b+\tau/4c^2}] - \kappa_l \frac{\epsilon}{A} \left( \frac{\sigma}{R_0} \right)^6 \frac{1}{\left( 1 + \frac{b}{\alpha R_0} \right)^6} \\
& - \frac{a_3 \tau^2}{c^6} \left[ e^{-2b+\tau/c^2} - \frac{1}{4} e^{-b+\tau/4c^2} \right]^2 + \frac{P(\alpha R_0 + b)^3}{\sqrt{2} A \alpha^3},
\end{aligned} \tag{3}$$

where  $b = \alpha(R - R_0)$  represents the reduced lattice expansion,  $R$  is the nearest-neighbor distance,  $z = 12$  is the coordination number,  $P$  is the external pressure,

$$\Lambda = \frac{\hbar \alpha}{\sqrt{MA}} \tag{4}$$

is the de Boer parameter for the Morse potential,  $M$  and  $N$  are the atomic mass and the total number of atoms.

The first term in Eq. (3) determines the entropy part of the free energy of vibrations of an atom of the crystal, the second term represents the average potential energy of interaction of nearest neighbors. While the short-range interaction of neighboring atoms is given by the Morse potential, the long-range Van der Waals attraction ( $\sim -r^{-6}$ ) between an atom and the atoms other than its nearest neighbors is described by the attractive part of the Lennard-Jones potential with the parameters  $\epsilon$  and  $\sigma$ . This interaction is taken into account by the third term in Eq. (3), with  $\kappa_l = 4.91$  for the RGC.<sup>11</sup>

The fourth term in Eq. (3) determines a contribution to the free energy of the crystal due to the cubic anharmonicity of collective atomic vibrations, evaluated in the second order of the perturbation theory, with  $a_3 \approx 2.31$ . This correction is rather small and contributes relatively little to the free energy (3). However, its strong temperature dependence, especially in the vicinity of the melting point, is responsible for the peculiar high-temperature behavior of a number of thermodynamic parameters, such as specific heat, thermal expansion, Grüneisen parameter, etc.

Thermodynamic potential (3) is a function of reduced temperature  $\tau$  and external pressure  $P$ . Two internal crystal parameters  $b$  and  $c$ , representing the lattice expansion and the dimensionless effective quasielastic bond constant, are considered as variational parameters minimizing the crystal free energy at the given temperature and pressure. The temperature range, where Eq. (3) holds, is determined by the inequality  $\tau \gg c\Lambda$ .

As in Ref. 5, the values of the parameters of the Morse potential  $A$ ,  $R_0$ , and  $\alpha$  are determined to fit the experimental values of the sublimation energy, the interatomic spacing, and the bulk modulus of the RGC at zero temperature and pressure. Incorporation of the long-range attraction of atoms results in an additional compression of the lattice in comparison with the system with the nearest-neighbor interaction only. Taking the compression into account is important in examination of the vacancy structure. The values of the parameters  $A$  and  $R_0$  of the RGC determined in this model are

TABLE I. Parameters of the Morse and Lennard-Jones potentials for the RGC.

	$\alpha$ ( $\text{\AA}^{-1}$ )	$A$ (K)	$R_0$ ( $\text{\AA}$ )	$\sigma$ ( $\text{\AA}$ )	$\epsilon$ (K)
Ne	2.04	38	3.15	2.74	36
Ar	1.63	117	3.83	3.4	121
Kr	1.52	172	4.09	3.65	164.5
Xe	1.38	226	4.46	3.98	232

different from those obtained in Ref. 5, where the long-range interatomic interaction was not considered. However, the agreement of the thermodynamic properties and the equation of state of the perfect RGC calculated within the present model with the observed data is as good as in Refs. 5–7. The values of the parameters  $A$ ,  $R_0$ , and  $\alpha$  for the RGC are listed in Table I together with the parameters of the Lennard-Jones potential.<sup>11</sup>

As emphasized in Ref. 5, the drastic decrease of the equilibrium value of the quasielastic bond parameter  $c_0(\tau)$  as the temperature approaches the melting point is an indicative of the vicinity of the instability point  $\tau_c$ , where the free energy minimum with respect to parameter  $c$  disappears. This instability is directly related to the vibrational anharmonicity, manifesting itself in the attraction between phonons, which is enhanced with temperature. As the system approaches the critical temperature  $\tau_c$ , where  $dc/d\tau \rightarrow -\infty$ , the phonon concentration  $\bar{n}$  increases with an infinite rate,  $d\bar{n}/d\tau \rightarrow \infty$ . As a result, the system's thermal susceptibility becomes anomalously large, manifesting itself in a nonlinear rise of specific heat, linear expansion coefficient, etc. For heavy RGCs we obtain  $\tau_c = 0.71$ , and for Ne  $\tau_c = 0.65$ . The formation energy of structure defects should also be sensitive to the proximity to the instability point.

The appearance of a vacancy in the lattice results in substantial distortion of the distribution of displacements of atoms surrounding the vacancy. The presence of an empty site primarily affects the atomic distribution in four coordination spheres of the vacancy. In fact, each atom of the first coordination sphere has one broken bond. This results in weakening of its repulsion in the direction of the vacant site, which, in turn, leads to an elongation of the atomic distribution and a shift of the center of the distribution towards the vacancy. Each atom of the second coordination sphere of the vacancy is affected by the deformation of the atomic distribution of four nearest neighbors of the vacancy, each atom of the third coordination sphere is affected by two atoms, and, finally, each atom of the fourth coordination sphere is affected by one atom of the first coordination sphere of the vacancy. For symmetry reasons, the distribution functions of displacements of an atom belonging to  $n$ th coordination sphere of the vacancy is symmetrical about the direction to the vacancy and is written as

$$f(x, y, z) = C_n \exp \left\{ -\frac{2\alpha^2}{\tau} [c_{n1}^2 x^2 + c_{n2}^2 (y^2 + z^2)] \right\}, \tag{5}$$

where  $c_{n1}$  and  $c_{n2}$  are the variational parameters that characterize, respectively, the longitudinal and the transverse

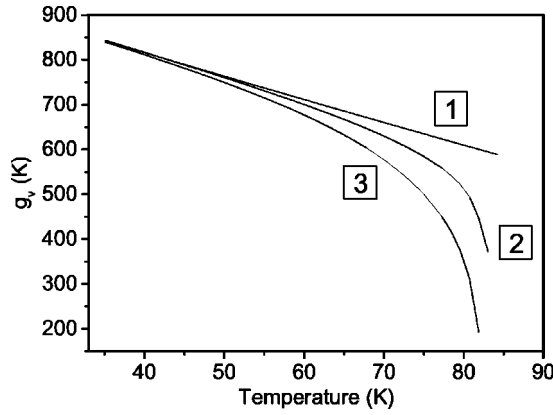


FIG. 1. The free energy of the vacancy formation in solid Ar at zero pressure calculated up to the instability point. Curve 1 was obtained in the quasi-harmonic approximation taking into account the relaxation of atoms of four coordination spheres of the vacancy. Curves 2 and 3 were computed within the model with the cubic anharmonicity taken into account, including the relaxation of atoms of two and four coordination spheres of the vacancy, respectively.

widths of the distribution. The  $x$  axis is chosen to pass through the sites of the atom and the vacancy.

The change of the distribution of the atomic displacements causes a change of the energy of interaction between the atoms around the vacancy and with the atoms of their own surrounding. For example, the change of interaction between the atoms of the vacancy's first coordination sphere is

$$\Delta U = A \frac{z_1 z_{11}}{2} \left[ \exp\left(-2b_1 + \frac{\tau}{4c_{11}^2} + \frac{3\tau}{4c_{12}^2}\right) - 2 \exp\left(-b_1 + \frac{\tau}{16c_{11}^2} + \frac{3\tau}{16c_{12}^2}\right) - \exp\left(-2b_0 + \frac{\tau}{c_0^2}\right) + 2 \exp\left(-b_0 + \frac{\tau}{4c_0^2}\right) \right], \quad (6)$$

where  $z_{11}=4$  is the number of common neighbors of

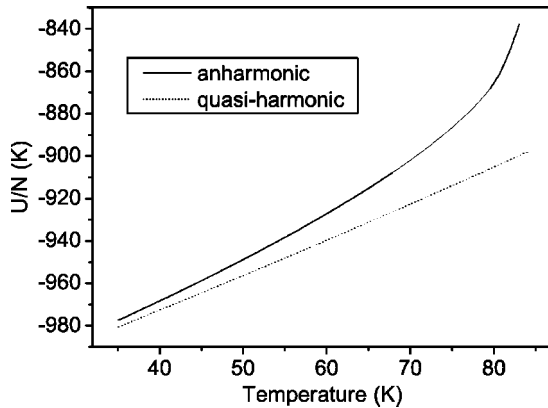


FIG. 2. Average potential energy per atom of solid Ar calculated within the quasiharmonic model (dotted line) and taking the cubic anharmonicity into account (solid line).

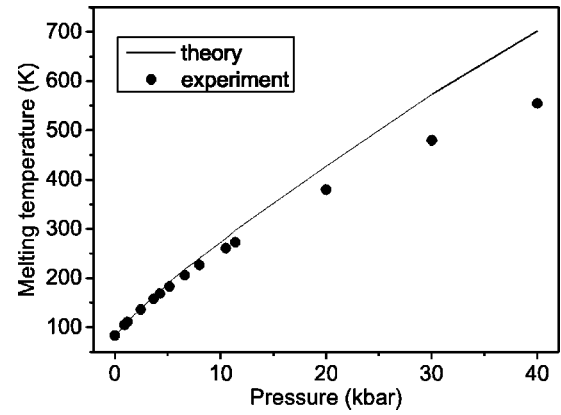


FIG. 3. Melting curve of Ar. Experimental values are from Refs. 12 and 13.

both vacancy and one of the atoms of its first coordination sphere,  $b_0$  is the equilibrium value of the parameter of lattice expansion calculated for a perfect solid,  $b_1 = \alpha(R_{11} - R_0)$ ,  $R_{11}$  is the distance between the vacant site and one of its neighbors shifted towards the vacancy. Similar to Eq. (6), we should take into account the changes of the average potential energy of interaction of all the atoms belonging to the first, second, third, and fourth coordination spheres of the vacancy with their own nearest neighbors. In addition to the change of the potential energy of interatomic interaction, the total change of the crystal free energy due to the vacancy formation includes the change of the entropy term given by

$$\Delta \Phi_s = A \tau \sum_{n=1}^4 z_n \ln \left[ \frac{c_{n1} c_{n2}^2}{c_0^3} \right], \quad (7)$$

where  $z_n$  is the number of atoms in  $n$ th coordination sphere of the vacancy.

To obtain the free energy of the medium relaxation, we minimize the total change of the crystal free energy with respect to parameters  $c_{n1}$ ,  $c_{n2}$ , and  $b_1$ . The sum of the free energy of the medium relaxation and the work required to remove an atom from a lattice site constitutes the free energy  $g_v$  of the vacancy formation. In Fig. 1 we plotted the temperature dependence of the free energy of the vacancy formation in solid Ar at zero pressure. In the same plot we show the curve computed within the quasiharmonic model without regard for the cubic anharmonicity contribution to the free energy. The comparison of these curves suggests that it is the vibrational cubic anharmonicity that is responsible for the dramatic decrease of the vacancy formation energy near the melting point. To understand the reason for such behavior of  $g_v$ , let us compare the average potential energy of interatomic interaction calculated for both quasiharmonic and anharmonic perfect crystals (Fig. 2). Figure 2 demonstrates that the cubic anharmonicity gives rise to the accumulation of an excess of the potential energy of the perfect crystal near the instability temperature. Generation of the structure defects breaks the translational symmetry of the crystal, and the relaxation brings the medium around the defects out of the instability region. The accumulated energy

excess is released through the medium relaxation and reduces the defect formation energy. Therefore, defects of structure (vacancies, dislocations, etc.) in an anharmonic crystal should be treated as centers of relaxation of the excessive potential energy. The next conclusion is that, since the defect formation energy in the anharmonic crystal tends to zero as temperature increases, the phase with a high concentration of defects becomes thermodynamically favorable. It seems natural to identify the new phase with a liquid.

The above argument allows one to conclude that the melting temperature of the RGC is directly related to the temperature range  $\tau \rightarrow \tau_c$ , where the system approaches the point of the instability of the crystalline state. In Fig. 3 we show the melting curve of Ar calculated from the condition that the system reaches the instability point.

The discrepancy between the theoretical and the observed values at high pressure seems, to our opinion, to be attributed to a more complicated mechanism of creation of the structure defects in a compressed medium, that may result in peculiar behavior of the melting curves of various substances at high pressures.<sup>14,15</sup>

The character of behavior of the system near the instability region can be investigated experimentally by x-ray studies of the mean-square displacement of atoms of the crystal, which, within the present approach, is in the inverse proportion to the square of the quasielastic module and depends on the correlative broadening of the width of the atomic distribution

$$\frac{\langle q^2 \rangle}{R^2} = \frac{3\tau}{4c_0^2(\tau)(\alpha R)^2 g_t}. \quad (8)$$

Here  $g_t \approx 0.77$  is the total correlation smearing of the region of localization of an atom at  $\tau = \tau_c$  (see Ref. 5). On the other hand, Eq. (8) equals the square of the Lindemann parameter  $\delta$ . Our calculation gives  $\delta(\tau_c) = 0.098$  at  $P=0$ , in a good agreement with the Lindemann criterion for the RGC,<sup>16</sup> while the quasiharmonic model gives  $\delta(\tau_c) \approx 0.081$ .

In summary, our studies of the formation of vacancies in the RGC allow us to conclude that a steep decrease of the vacancy formation energy near the instability point of the crystalline state is directly related to the enhancement of the vibrational anharmonicity at high temperature. As vacancies appear, the accumulated potential energy excess is released through the relaxation of the medium around a vacancy, favoring a reduction of the vacancy formation energy. It should be noted that the vibrational anharmonicity should manifest itself also in the formation of the dislocation structure of the crystal and, thus, affect substantially the high-temperature strength and creep properties of crystals. It seems natural to suppose that the evolution of the solid state instability is related to the premelting effects in crystals.<sup>17</sup>

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