LATTICE DYNAMICS
AND PHASE TRANSITIONS

Theory of Isotope Effect in the Thermodynamics of "Classical" Crystals

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Received October 29, 2007

Abstract—Based on general expressions for quantum contributions to the free energy of a statistical system, an approach is developed making it possible to carry out a complete theoretical analysis of the equilibrium thermodynamic characteristics of argon-type crystals as a function of the isotopic mass. The theory is based on independently calculated (in fact, without fitting parameters) one-particle and two-particle distribution functions of the classical crystal and permits one to quantitatively describe the data on the lattice parameters of isotope crystals obtained from numerical experiments. It is pointed out that real experiments are needed to study the isotope effect in crystals of noble gases, especially in view of the fact that, according to the literature data, xenon undergoes an fcc–hcp phase transition under increased pressure.

The construction of a consistent theory of the crystalline state remains an important problem in fundamental physics [1]. This problem is of particular interest in view of the fact that the thermodynamic characteristics of crystals of different isotopes should differ [1, 2] and these differences are certain to be of a quantum nature. Although the magnitude of the isotope effect (e.g., for the lattice parameters) is expected to be fairly small (~10^{-3} Å), it can be measured by the modern experimental methods, as demonstrated in [3] for crystals of Si and Ge isotopes using x-ray diffraction. As for the influence of the isotopic composition on the thermodynamic characteristics of crystals of noble gases, we are aware of only one experimental study of ^{20}Ne and ^{22}Ne [4]. However, it is crystals of noble gases (and the corresponding simple liquids) that are the most convenient objects for studying the fundamental laws of the physics of the condensed state.

Since no experimental data are available in the literature on the isotope effect in argon-type crystals, computer simulations of the structural characteristics of such media are of importance. For example, in [5, 6], the temperature dependences of the thermodynamic characteristics (in particular, lattice parameters) of ^{20}Ne and ^{22}Ne crystals were modeled using the Monte Carlo method. In [7], this method was used to calculate the structural characteristics of an fcc lattice consisting of 500 atoms, which corresponded to real isotopes of Ar, Kr, and Xe. Thus, computer simulation is currently the only alternative to real experiments on the isotope effect in argon-type crystals.

It should be noted that the data from computer simulations were theoretically interpreted in [7] using semiquantitative estimates based on a quasi-harmonic approximation with appropriate values of the Grüneisen constant and the maximum Debye phonon frequency. However, there is a method that enables one to quantitatively describe in detail the specific features of the isotope effect in Ar-type crystals without making highly restrictive assumptions. This method is based on the ideas behind the statistical theory of crystalline media and has been successfully used to quantitatively describe (in fact, without adjustable parameters) experimental crystal–gas phase equilibrium curves for "classical" media (such as argon) [8] and for media (such as neon) with noticeable quantum effects [9].

In this study, we develop a statistical theory of the isotope effect in classical Ar-type crystals in which the main quantum correction to thermodynamic characteristics can be found self-consistently from the one-particle and two-particle distribution functions of atoms in the classical crystal. We show that the theoretical results obtained are in good quantitative agreement with the results of computer simulations [7] for crystals of the Ar, Kr, and Xe isotopes over a wide temperature range. The quantum correction found for Ne leads to overestimated values (in comparison to the results of computer simulations [5]) at temperatures below the triple point in the sublimation curve; therefore, higher order terms in $\hbar$ should be taken into account. However, with increasing pressure and (or) temperature, a crystalline state arises on the phase diagram for which the calculated correction (~$\hbar^2$) determines the main part of the isotope effect for neon as well.
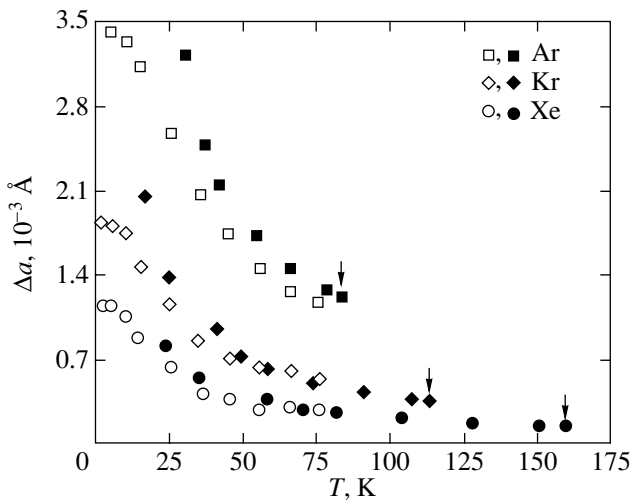
Temperature dependences of the differences between the quantum corrections to the crystal lattice parameters of the extreme isotopes of Ar (^{36}Ar, ^{40}Ar), Kr (^{78}Kr, ^{86}Kr), and Xe (^{124}Xe, ^{136}Xe). The values of Δa calculated using our theory are shown by solid symbols, and the data from computer simulations [7], by open symbols. The arrows indicate the triple points of the corresponding substances.

Let us calculate the quantum correction δa to the lattice parameter of a classical crystal. We use the general expression

$$V = \left(\frac{\partial \Phi}{\partial p}\right)_T, \qquad (1)$$

which relates the crystal volume V to the derivative of the thermodynamic potential $\Phi = F + pV$ (F is the free energy) with respect to the pressure p at a constant temperature T [10]. Assuming that the quantum correction δa is small as compared to the length a_0 of a cube edge for a Bravais lattice (fcc lattice for Ar-type crystals [11]), we can write

$$\delta a = \frac{4}{3a_0^2 N}\left(\frac{\partial \delta \Phi}{\partial p}\right)_T, \qquad (2)$$

where $\delta \Phi$ is the quantum correction to the thermodynamic potential and N is the total number of atoms in the volume V. In deriving Eq. (2), we took into account that the unit cell of an fcc lattice contains four atoms [10]. According to the theorem of small corrections [10], the correction $\delta \Phi$ and the quantum correction δF to the free energy should coincide if they are expressed in terms of the corresponding variables. Therefore, knowing the dependences of the parameters involved in δF on pressure and temperature, we can determine the quantum correction to the chemical potential $\delta \mu =$

$\delta \Phi / N$. Using an explicit expression for δF [9], we obtain

$$
\begin{aligned}
\delta \mu = \frac{\Lambda^{*2} w_0}{16\pi^2 T^*}\Bigg\{ & \frac{8\pi^{5/2}\sigma^3}{3\beta^{3/2}} \int_0^\infty d\xi \frac{d}{d\xi}\left[\xi^2 \frac{d\hat{W}(\xi)}{d\xi}\right] \\
& \times \frac{1}{Y + (1-Y)\exp[4\hat{W}(\xi)/T^*]} e^{-\pi^2\sigma^2\xi^2/\beta} \\
& + \frac{2\sqrt{\pi}\sigma^2}{3\sqrt{\beta}} \sum_{\hat{\mathbf{h}}\neq 0} \frac{1}{\hat{h}}\int_{-\infty}^\infty \frac{d\xi}{\xi}\frac{d}{d\xi}\left[\xi^2\frac{d\hat{W}(\xi)}{d\xi}\right] \\
& \times \frac{1}{Y+(1-Y)\exp[4\hat{W}(\xi)/T^*]} e^{-\pi^2(\hat{h}-\sigma\xi)^2/\beta}\Bigg\},
\end{aligned}
\qquad (3)
$$

where the parameters β, σ, and Y (their definitions can be found in [8, 9]) are assumed to be expressed in terms of the dimensionless pressure $p^* = pD^3/w_0$ and the dimensionless temperature $T^* = T/w_0$, and D and w_0 are the characteristic parameters of the Lennard–Jones potential, which can be written in a dimensionless form as $\hat{W}(\xi) = \xi^{-12} - \xi^{-6}$. In Eq. (3), $\Lambda^* = 2\pi\hbar/(D\sqrt{mw_0})$ is the de Buhr quantum parameter [11] (m is the atomic mass), and the summation is over all dimensionless vectors $\hat{\mathbf{h}}$ related to the fcc lattice vectors $\mathbf{a}$ by the equation $\hat{\mathbf{h}} = \sqrt{2}\mathbf{a}/a_0$ [9].

We calculated the quantum correction to the lattice parameter of Ar-type crystals in the vicinity of the sublimation curve (as in computer simulations in [7]) for dimensional temperatures $T^* = 0.10$, 0.15, 0.25, 0.35, 0.45, 0.55, 0.65, and 0.6875 (the last value corresponds to the triple point for crystals of noble gases [11]) using the procedure described in [8] (see also [9]). For each temperature, we found the values of β, σ, and Y (and, accordingly, $\delta \mu$) at two somewhat different pressures p_1^* and p_2^* in the vicinity of $p^* \approx 0$ and then calculated the derivative in Eq. (2) as the ratio of the corresponding finite differences (in [8], the isothermal compressibility was calculated in the same manner).

Table 1 lists the calculated values of the "universal" factor in the quantum correction to the chemical potential at the two pressure values (specified by subscripts 1 and 2) and the values of the universal factor in the quantum correction to the lattice parameter of the crystal.

The data presented in Table 1 are used to analyze the isotope effect in Ar, Kr, and Xe crystals. In accordance with the data from computer simulations [7], we constructed the temperature dependences of the differences Δa between the quantum corrections to the lattice parameters of the extreme isotopes of Ar (^{36}Ar, ^{40}Ar), Kr (^{78}Kr, ^{86}Kr), and Xe (^{124}Xe, ^{136}Xe).

The figure shows the theoretically calculated values of Δa (solid symbols) and the data from computer simulations [7] (open symbols). We note, above all, that the

Table 1. Universal factor in the expression for $\delta\mu$ calculated for two somewhat different pressures (specified by subscripts 1 and 2) and the universal factor in δa at various temperatures

T^*	$10^2 p_1^*$	$\dfrac{\delta\mu_1}{\omega_0 \Lambda^{*2}}$	$10^2 p_2^*$	$\dfrac{\delta\mu_2}{\omega_0 \Lambda^{*2}}$	$\dfrac{1}{\omega_0 \Lambda^{*2}}\dfrac{\partial\delta\mu}{\partial p^*}$
0.1	1.13611	11.2070	−1.09502	11.1850	0.986047
0.15	1.09478	7.42174	−0.928794	7.40824	0.667138
0.25	1.08411	4.37304	−1.24564	4.36247	0.453697
0.3	1.23046	3.65262	−0.797357	3.64552	0.350129
0.35	1.30006	3.10186	−0.998933	3.09484	0.305279
0.45	1.34371	2.36979	−1.55284	2.36266	0.246155
0.55	0.748081	1.89987	−0.127892	1.89803	0.210052
0.65	1.15836	1.57590	−1.32958	1.57129	0.185294
0.6875	0.432636	1.47368	−0.729596	1.47161	0.178106

Table 2. Calculated Δa values for crystals of the extreme Ar, Kr, and Xe isotopes at various pressures

Δa	$T^* = 0.55$				$T^* = 0.65$			
	$p^* = 0$	$p^* = 11.8$	$p^* = 23.7$	$p^* = 29.5$	$p^* = 0$	$p^* = 11.8$	$p^* = 23.7$	$p^* = 29.5$
$\Delta a_{Ar} \times 10^{-3}$	1.45	1.10	1.02	1.01	1.27	0.928	0.870	0.853
$\Delta a_{Kr} \times 10^{-4}$	4.21	3.20	2.98	2.92	3.68	2.69	2.52	2.47
$\Delta a_{Xe} \times 10^{-4}$	1.66	1.26	1.17	1.15	1.45	1.06	0.995	0.975

best agreement between our theory and the data from [7] is achieved for crystals of heavy elements, for which the calculated quantum correction adequately describes the isotope effect down to very low temperatures (this is particularly true for Xe crystals). For argon, the agreement between our theory and the data from [7] is somewhat worse and, as we might expect, the discordance increases with decreasing temperature.

The calculated value of the isotope effect in the neon crystal proves to be noticeably higher than the experimental values obtained for a neon crystal in equilibrium with the vapor in real [4] and numerical [5, 6] experiments over the entire temperature range up to the triple point. Therefore, the calculated quantum correction is not the only contribution to the isotope effect in neon crystals under saturation vapor pressure. We also calculated the next-order correction (proportional to $\hbar^3$), but its numerical value proved to be small, as in the case of sublimation [9]. It is not an aim of this study to calculate the correction proportional to $\sim\hbar^4$; however, it should be noted once again that, at increased pressures and (or) temperatures, our theory can quantitatively describe the isotope effect in neon crystals as well.

In [7], in addition to computer simulations of crystals under zero pressure, the pressure dependence of Δa was simulated for model fcc crystals of noble gases in the quantum temperature range (at $T = 5$ K). We calculated this dependence at dimensionless temperatures $T^* = 0.55$ and 0.65, at which our theory adequately

describes the isotope effect. Table 2 lists the values of Δa for the extreme isotopes of Ar, Kr, and Xe at dimensionless pressures up to $p^* = 29.5$. The calculated pressure dependences are in qualitative agreement with those found in [7], and the numerical values of Δa exhibit a natural tendency to decrease with increasing temperature.

For xenon, the value $p^* = 29.5$ (Table 2) corresponds to a pressure of 15.1 kbar (1.51 GPa). It is interesting that, at such pressures, x-ray diffraction studies [12] revealed signs of an fcc–hcp phase transition in Xe crystals. Therefore, the isotope effect should be studied with allowance for this phase transition, at least for xenon. One might expect that a consistent statistical theory of the crystalline state will predict the occurrence of this phase transition. We plan to analyze this problem in a future publication.

Quantum corrections should manifest themselves not only in the lattice parameter but also in other thermodynamic characteristics of crystals, e.g., in the bulk modulus. The corresponding isotope effect can be calculated in much the same manner as above. However, since experimental data on the compressibility of crystals of different isotopes are absent in the literature, we do not present these calculation here.

Thus, we have developed a theory that makes it possible to quantitatively describe (in fact, without fitting parameters) the computer simulations data [7] on the temperature and pressure dependences of the isotope

effect in classical argon-type crystals. The best agreement has been achieved for crystals of heavier elements. It is important to perform real experiments on the isotopic effect, especially in the pressure range where the fcc–hcp phase transition was detected in Xe in [12]. Such experiments would stimulate further theoretical studies of quantum corrections to the thermodynamic functions of crystals with primitive unit cells containing more than one atom.

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Translated by Yu. Epifanov

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