VACANCY EQUILIBRIUM CONCENTRATION OF ANHARMONIC CRYSTALS UNDER PRESSURE.

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ıct: The Gibbs energy change on forming a simple vacancy is determined. The y equilibrium concentration of the face - centered cubic crystals. N_ν are considered. xpression of N_ν at various pressure is obtained. Specific heat, compressibility ients X_T and X_S, linear thermal expansion coefficient are calculated and compared xperimental data for Ar crystal with point defects. Our numerical results are also red with Zubov's one.

I. INTRODUCTION.

ıe thermodynamic properties of anharmonic crystals were considered by the mo- method in [1]. The point defects in crystals play the important role for these ·ties and were investigated by many authors [2,3,4,5,6,7,8].

the works [6,7,8] the anharmonic crystals with lattice defects were considered by ɔment method. In this paper we consider crystals with point defects at various res and obtain the analytic expression for vacancy equilibrium concentration de- ıg on pressure. From this we can have the expression for C_ν, C_p., X_ν, X_S, α. The ical calculation results for inert gas crystal Ar at pressures $0, 5.10^5$ Kpa and 1.10^5 re in concordance with experimental data.

:XPRESSION OF THE VACANCY EQUILIBRIUM CONCENTRATION FOR CRYSTALS WITH POINT DEFECTS.

ɔnsider the crystal containing N atoms, in which there are n vacancies. If only take ccount the interaction of particles being on the first and the second coordination s, we have the Helmholtz free energy ψ [7]:

$$\psi = [N - (n_1 + n_2)n]\psi_0 + nn_1\psi_1 + nn_2\psi_2 + n(B - 1)\psi_0 \tag{1}$$

re, n_1 and n_2 are particles being on the two first coordination spheres; ψ_0 is the ıergy of one particle in the ideal crystal [1]; ψ_1 and ψ_2 are the free energy of one le being on the first coordination sphere and the second one containing one vacancy; $)\psi_0$ is the free energy change of a particle when leaving from the node of a lattice ming a single vacancy.

he vacancy concentration is determined from[2,5]

$$N_\nu = \frac{n}{N} = \exp\{-\frac{g_\nu^f}{\theta}\} \tag{2}$$

g_ν^f is the Gibbs energy change on forming a simple vacancy and equal

$$g_\nu^f = G(P,T) - G_0(P,T) \tag{3}$$

$$G_0(P,T) = N\psi_0 + PV_0 .$$

is the Gibbs free energy of the ideal crystal containing N atoms in volume V_0; $G($ one of the real crystal having a vacancy and the volume V. Using (1), (2 and easily have.

$$g_\nu^f = -(n_1+n_2)\psi_0 + n_1\psi_1 + n_2\psi_2 + (B-1)\psi_0 + P(V-V_0)$$

From the condition $N_\nu < 1$ we can find:

$$1 < B < \frac{-(n_1+n_2)\psi_0 + n_1\psi_1 + n_2\psi_2 - \psi_0}{-\psi_0}$$

The parameter B can be found by comparing experimental values of N_ν near th ing temperature with theoretical values calculated from (2) , For simplicit;, we approximation expression for B by an arithmetic averaging:

$$B \cong 1 + \frac{(n_1+n_2)\psi_0 - n_1\psi_1 - n_2\psi_2}{\psi_0}$$

Using (1) and thermodynamic relation

$$PV = -\frac{a}{3}(\frac{\partial\psi}{\partial a})_T$$

Where a is the nearest neighbour distance between two atoms, we have:

$$PV = PV_0 - \frac{a}{3}\frac{\partial}{\partial a}(n\frac{\partial\psi}{\partial n}) \qquad PV = PV_0 - \frac{a}{3}\frac{\partial n}{\partial a}\frac{\partial\psi}{\partial n} - \frac{an}{3}\frac{\partial^2\psi}{\partial a\partial n}$$

From (1), (2) and (4) we can find

$$\begin{aligned}\frac{a}{3}\frac{\partial n}{\partial a}\frac{\partial\psi}{\partial n} &= -\frac{1}{\theta}[-(n_1+n_2)\psi_0 + n_1\psi_1 + n_2\psi_2 + (B-1)\psi_0] \\ &\times [(n_1+n_2)\frac{PV_0}{N} - n_1\frac{PV_1}{N} + n_2\frac{PV_2}{N} + (B-1)\frac{PV_0}{N}] \equiv \hat{A} \\ \frac{an}{3}\frac{\partial^2\psi}{\partial a\partial n} &= [-an\frac{\partial(PV)}{\partial n}] = \frac{1}{X_T}\frac{\partial Y}{\partial a}\frac{\partial a}{\partial n} - a^2P\sqrt{2}N\frac{\partial a}{\partial n}\end{aligned}$$

here X_T is the isothermal compressibility coefficient of the crystal. In [6,7] $\frac{\partial a}{\partial n}$ is

$$\frac{\partial a}{\partial n} = \frac{1}{N}[-(n_1+n_2)y_0 + n_1y_1 + n_2y_2]$$

Where, y_0 is the displacement of a particle from the equilibrium positio in tl crystal; y_1 (or y_2) the one in the crystal having a defect being on the first coord sphere (or the second). Therefore, the expression of g_ν^f is:

$$g_\nu^f = \Delta\psi - \hat{A} - [-(n_1+n_2)y_0 + n_1y_1 + n_2y_2](\frac{3}{2X_T} - P)\sqrt{2}a^2)$$

$$\Delta\psi = \psi - N\psi_0$$

and we have the expression of N_ν depending pressure:

$$N_\nu = \exp\{-\frac{\Delta\psi}{\theta}\}\exp\{\frac{1}{\theta}[-(n_1+n_2)y_0 + n_1y_1 + n_2y_2](\frac{3}{2X_T} - P)\sqrt{2}a^2)\}\exp\{\frac{\hat{A}}{\theta}\}$$

ystals we always have $\frac{A}{\theta} \ll 1$, so we can write (12) as following:

$$N_\nu = N_\nu(P=0)\exp\{\frac{1}{\theta}[-(n_1+n_2)y_0 + n_1 y_1 + n_2 y_2](\frac{3}{2X_T} - P)\sqrt{2}a^2)\} \qquad (13)$$

$$N_\nu = N_\nu(P=0)\exp\{-\frac{-(n_1+n_2)\psi_0 + n_1\psi_1 + n_2\psi_2 + (B-1)\psi_0}{\theta}\}$$

the thermodynamic relations and the expression of the free energy ψ (1), the sion of the vacancy equilibrium concentration we can find specific heat C_ν, C_p., othermal compressibility and adiabatic compressibility coefficients X_T and X_S, the expansion coefficient α of crystals at the various pressures. In the following para-, we shall apply these results to our investigation of the inert gas crystal Ar at the ire $0,5.10^5$ Kpa and 1.10^5 Kpa.

III. THERMODYNAMIC PROPERTIES OF THE CRYSTAL A_r WITH DEFECT AT THE PRESSURE 0,5. 10^5 Kpa AND 1.10^5 Kpa.

he interaction potential between two atoms of an inert gas is often used in the form : Lennard-Jones one. In the case of the crystal argon we have the experimental $r = 3,405.10^{-10}$m , $\epsilon/k_B = 119,8^0$ [8]. As in [1,7] and from the formulae (6), (13) we he values of the vacancy equilibrium concentration, the thermodynamic quantities X_T, X_S, α at the pressures $0,5.10^5$ Kpa and 1.10^5 Kpa. The results are written in ables 1 and 2. We also write the results of the calculation by the moment method e ideal crystal [1], by the one particle distribution function method of Zubov [9] he experimental data [10].

the vicinity of the melting temperature, the vacancy equilibrium concentration is small ($\sim 10^{-3}$) and the discrepancy of the thermodynamic quantities in comparison experiments is of some percent.

rom the numerical result we see that the vacancy equilibrium concentration at ame temperature is decreased when the pressure is risen. The good concordance e theoretical calculations and the experimental data (the error $\sim$ some percent) that we can use the moment method in investigating crystals with defects at the us pressure. This publication is completed with financial support from National Research Program in Natural Sciences.

Table 1: Thermodynamic properties of Ar with defect at pressure $0,5.10^5$ Kpa.

, K	30	40	50	60	70	80	90
N_ν	$6,33.10^{-6}$	$1,31.10^{-4}$	$2,57.10^{-4}$	$7,84.10^{-4}$	$1,5.10^{-3}$	$1,84.10^{-3}$	$1,62.10^{-3}$
10^{-10} m)	3,734	3,748	3,7634	3,7804	3,79996	3,8216	3,8475
MM[1]	3,734	3,748	3,7634	3,7804	3,79996	3,8217	3,8476
bov [9]				3,7859		3,8222	
xp[10]	3,7426	3,7529	3,7650	3,7793	3,7954	3,8137	3,8349
$0^{10}Pa^{-1}$)	3,33	3,61	3,95	4,39	4,94	5,71	6,70
MM[1]	3,33	3,61	3,95	4,38	4,92	5,69	6,65
bov [9]				4,88		6,21	
xp[10]	3,47	3,85	4,15	4,52	5,00	5,59	6,49

T^0, K	30	40	50	60	70	80	
N_V	$6,33.10^{-6}$	$1,31.10^{-4}$	$2,57.10^{-4}$	$7,84.10^{-4}$	$1,5.10^{-3}$	$1,84.10^{-3}$	1,6
$X_S(10^{-10}Pa^{-1})$	3,12	3,27	3,45	3,66	3,93	4,27	4
IMM	3,12	3,27	3,45	3,68	3,97	4,35	4
Zubov [9]				4,00		4,57	
Exp [10]	3,40	3,51	3,64	3,79	3,97	4,18	4
$\alpha(10^{-4}k^{-1})$	2,72	3,20	3,58	3,97	4,41	5,01	5
IMM [1]	2,72	3,20	3,58	3,96	4,40	5,00	5
Zubov [9]				4,24		5,37	
Exp [10]	2,39	2,98	3,45	3,91	4,57	4,98	5
$C_V(JK^{-1}mol^{-1})$	19,07	20,99	21,87	22,30	22,47	22,55	2
IMM [1]	19,07	20,99	21,87	22,29	22,46	22,54	2
Zubov [9]				21,22		21,59	
Exp [10]	16,84	19,65	21,12	21,91	22,29	22,50	2
$C_P(JK^{-1}mol^{-1})$	20,36	23,21	25,06	26,76	28,26	30,08	3
IMM [1]	20,36	23,21	25,06	26,52	27,86	29,46	3
Zubov [9]				25,83		29,47	
Exp [10]	17,81	21,54	24,05	26,10	27,57	30,04	3

Table 2: Thermodynamic properties of A_r with defect at pressure 1.10^5 Kpa

T^0K)	30	40	50	60	70	80	90	
N_V	$6,15.10^{-6}$	$1,22.10^{-4}$	$2,27.10^{-4}$	$6,68.10^{-4}$	$1,74.10^{-3}$	$3,17.10^{-3}$	$1,56.10^{-3}$	2
$a(10^{-10})$	3,7143	3,7270	3,7409	3,7557	3,7721	3,7907	3,812	
IMM[1]	3,7143	3,7270	3,7409	3,7557	3,7722	3,7909	3,813	
Zubov 9]				3,7557		3,7879		
Exp [10]	3,7211	37301	3,7406	3,7526	3,7661	3,7810	3,797	
X_T $(10^{-10}Pa^{-1})$	2,94	3,17	3,51	3,75	4,14	4,64	5,24	
IMM[1]	2,94	3,17	3,51	3,74	4,11	4,59	5,22	
Zubov [9]				4,03		4,85		
Exp [10]	3,15	3,34	3,57	3,83	4,13	4,52	5,00	
$X_S(10^{-10}Pa^{-1})$	2,78	2,89	3,12	3,21	3,40	3,64	3,91	
IMM	2,78	2,89	3,12	3,21	3,41	3,66	3,97	
Zubov [9]				3,42		3,77		
Exp [10]	3,01	3,09	3,18	3,30	3,40	3,56	3,73	
$\alpha(10^{-4}k^{-1})$	2,35	2,78	3,02	3,38	3,71	4,11	4,56	
IMM [1]2,35	2,78	3,02	3,38	3,69	4,07	4,54	5,20	
Zubov [9]				3,35		4,24		
Exp[10]	2,05	2,57	2,97	3,32	3,67	4,05	4,49	

)	30	40	50	60	70	80	90	100
	$6,15.10^{-6}$	$1,22.10^{-4}$	$2,27.10^{-4}$	$6,68.10^{-4}$	$1,74.10^{-3}$	$3,17.10^{-3}$	$1,56.10^{-3}$	$2,04.10^{-3}$
mol^{-1})	18,56	19,73	21,20	22,00	2,19	22,24	22,19	22,06
[1]	18,56	19,73	21,20	22,00	22,17	22,21	22,17	22,04
ov				21,14		21,68		
[10]	16,34	19,32	20,82	21,66	2,12	22,38	22,50	22,54
mol^{-1})	19,65	21,66	23,88	25,71	26,98	28,32	29,77	31,70
[1]	19,65	21,66	23,88	25,60	26,73	27,86	29,16	30,07
v [9]				21,95		27,84		
[10]	17,10	20,87	23,34	25,18	26,82	28,41	30,13	32,14

IMM/L ideal moment method

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NGHIÊN CỨU QUÁ TRÌNH BIẾN ĐỔI NĂNG LƯỢNG TỰ DO KHI TẠO THÀNH MỘT VACANCY.

Vũ Văn Hùng và CTG

Đại học Sư phạm - ĐHQGHN

ghiên cứu nồng độ vacancy cân bằng N_v đối với các tinh thể lập phương tâm diện t ra được biểu thức đối với N_v ở các áp suất khác nhau. Tính được nhiệt dung, nén X_T và X_S hệ số dãn nở tuyến tính , và thực hiện so sánh với các số liệu thực m đối với A_r có khuyết tật điểm. Các kết quả tính số của chúng tôi cũng được so với các kết quả của Zubov.