

ANHARMONIC CONTRIBUTIONS TO VIBRATIONAL THERMODYNAMIC PROPERTIES OF IDEAL RARE-GAS CRYSTALS

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(Received October 1, 1983)

Using Singh's and Neb's potential, as a model of nearest neighbour central force interactions, the Helmholtz free energy, internal energy and specific heat at constant volume of ideal rare-gas crystals are evaluated in anharmonic approximation. The calculations are extended from the low to high temperatures.

Temperature dependences of the cubic and quartic anharmonic contributions to the thermodynamic functions are showed too.

Obtained results are compared with available experimental and other theoretical data.

Introduction

The rare-gas crystals (RGC) are prototype of molecular crystals [1]. They crystallize in simple close-packed arrangements to be expected for atoms with spherical symmetry [2]. The lattice atoms interact with weak forces principally Van der Waals (V-d-W) attractions [3]. The existence of the V-d-W attraction terms necessitates the consideration of an additional repulsive energy to stabilize the crystal lattice of the spherical atom. This repulsive interaction is short-range and overlap dependent in nature.

Earlier results and theoretical calculations of the short-range repulsion and the long-range attractive portion for a variety of pairwise interactions of atoms in the RGC have been reviewed in the articles by POLLACK [3] and HORTON [4] and in the book of GOODISMAN [5]. Recently the critical analysis of the potential energy curves (PEC) appropriate for the RGC has been given by SINGH and NEB [6] who proposed new model PEC. Singh's and Neb's (S—N) potential consists of the attractive V-d-W force (r^{-6}) modified by the three-body interactions arising from the variable induced dipoles and the repulsive Born—Mayer interaction. This model potential used to the calculation of the isothermal elastic constants and some thermodynamical properties of the RGC at temperature $T = 0$ K gave remarkably good agreement between theoretical and experimental results.

In this paper, using Singh's and Neb's PEC, we explore the temperature dependences of various thermodynamical functions like Helmholtz free energy F , internal energy U , specific heat at constant volume C_v as well as cubic and quartic contributions to the above thermodynamic quantities in the anharmonic approximation [7, 8].

The computed results in the high and low temperature limits have been compared with available experimental data [9—11] and theoretical results obtained in terms of the renormalized Morse potential in the reduced second-order self-consistent phonon approximation [12] as well as for the Mie—Lennard—Jones potential in the anharmonic approach [13, 14].

Thermodynamical functions of crystals

The Helmholtz free energy of a crystal in anharmonic approximation can be written as [14]:

$$F(T) = F_{qh}(T) + F_3(T) + F_4(T), \quad (1)$$

where: $F_{qh}(T)$ is the free energy in the quasi-harmonic approximation,

$F_3(T)$ and $F_4(T)$ are the cubic and quartic anharmonic contributions to the Helmholtz free energy.

As was shown in [7, 8] F_{qh} , F_3 and F_4 in the high ($\theta \gg \omega_L$) and low ($\theta \ll \omega_L$) temperature limits are respectively given by:

$$F_{qh} = 3RT \cdot FO, \quad (2)$$

$$F_3 = -0.056 N_A \theta^2 G, \quad (3)$$

$$F_4 = N_A K FQ, \quad \theta \gg \omega_L \quad (4)$$

and

$$F_{qh} = N_A FO, \quad (5)$$

$$F_3 = -0.7297 E_o \gamma G N_A, \quad (6)$$

$$F_4 = 0.75 N_A E_o K \cdot FQ, \quad \theta \ll \omega_L. \quad (7)$$

The symbols used in Eqs. (2)—(7) have the following meaning:

$$\theta = k_B T$$

$$\omega_L = \sqrt{8\hbar^2 \Phi''(r_e)/m}$$

$$\varphi''(r_e) = (\partial^2 \Phi(r)/\partial r^2)_{r=r_e},$$

$$G = (\Phi^{III}(r_e))^2 / (\Phi^{II}(r_e))^3,$$

$$K = \Phi^{IV}(r_e) / (\Phi^{II}(r_e))^2,$$

$$\gamma = \theta \left(\frac{T}{\theta_0} \right)^3.$$

$$\theta_0 = \theta_D [1 - 0.04166 E_h (1.2997 G - K)].$$

$E_o = E_h (1 - 0.04144 E_h G)$ is the zero-point energy per atom for the mean separation r_e in terms of its value $E_h = 1.0227 \omega_L$ evaluated at the minimum of the potential energy $\Phi(r)$ in the strict harmonic approximation.

R , N_A , k_B , \hbar , m and θ_D are the gas constant, Avogadro number, Boltzmann constant, Planck constant divided by 2π , mass of atom and Debye temperature in the harmonic approximation, respectively.

The specific heat at constant volume C_v and internal energy U are related to the Helmholtz free energy by [15]:

$$C_v = -T \left(\frac{\partial^2 F}{\partial T^2} \right)_v, \quad (8)$$

$$U = F - T \left(\frac{\partial F}{\partial T} \right)_v. \quad (9)$$

If we substitute Eqs. (1)–(7) into Eqs. (8) and (9) we find immediately that in the high and low temperature limits, respectively, C_v and U are equal to:

$$C_v \approx 3R(1 - CH(-0.04166\beta^2)), \quad (10)$$

$$U \approx 3RT(1 - UX) \text{ for } \theta \gg \omega_L, \quad (11)$$

and

$$C_v \approx \frac{12}{5} \pi^4 R \left(\frac{T}{\theta_0} \right)^3 (1 + CH), \quad (12)$$

$$U \approx N_A E_0(1 - UX) \text{ for } \theta \ll \omega_L, \quad (13)$$

where the exact expressions for FO , FQ , CH and UX for the high and low temperature limits are given in the Appendix.

Applying the results of Eqs. (1)–(13) we obtain the thermodynamic functions of solids if $\Phi(r_e)$ is known. We have chosen here the Singh's and Neb's PEC [6] to represent the interatomic potential between atoms in the rare-gas crystals.

$$\Phi(r_e) = C_1[1 + 12f(r_e)]/r_e^6 + 12b \exp(r_e/p), \quad (14)$$

$$\text{where: } C_1 = 14.4539 \text{ C,}$$

$$f(r_e) = f_0 \exp(-r_e/p).$$

C and b are the potential parameters which have been determined by help of the lattice constants and isothermal bulk modulus [6]. The other parameters p and $f(r_e)$ have been expressed from the knowledge of overlap integrals reported by Hafe-meister [16]. Numerical values of these parameters are collected in Table I.

Table I.

Singh and Neb potential constants for the pairwise atomic interactions in the RGC

Solids	Parameters			
	C $10^{-67} [\text{Jm}^6]$	b $10^{-19} [\text{J}]$	p $10^{-10} [\text{m}]$	$f(r_e)$
Ne	35.908	679.329	0.2393	0.000 23
Ar	611.06	2021.062	0.3056	0.001 71
Kr	1474.60	2561.60	0.3347	0.003 03
Xe	3334.05	3099.70	0.3706	0.005 82

Numerical results

Using the values of model parameters, reported in Table I, we have computed the quasi-harmonic (U_{qh}), cubic (U_3) and quartic (U_4) anharmonic contributions to the zero-point energy (Table II). Obtained results are compared with those calculated for the Morse renormalized potential [12] and (12—6) Mie—Lennard—Jones model [14]. Table III shows the comparison of the experimental data for the molar heat at constant volume C_v with calculated in terms of the above mentioned potentials. The experimental values of C_v for Ne, Ar and Kr were obtained from the equation: $C_v = C_p - 9\alpha^2 T / \kappa \rho$ using measured data [9—11] for all quantities on the right hand side of the equation in which C_p is the molar heat at constant pressure, α —the linear coefficient of thermal expansion, κ —the isothermal compressibility, ρ —the density. The calculation C_v for X_e was impossible because of on incomplete experimental data set.

It is evident from Table III that the values of molar heat at constant volume calculated for the S—N model potential are in good agreement with their measured data. Moreover, these results have shown improvements over those obtained by help of the M—L—J potential. This fact together with the results of paper [6] clearly demonstrates that a two-parameter model potential proposed by Singh and Neb is a good representation for the curve of the potential energy of the RGC.

The high temperature $\left(T > \frac{2}{3} \theta_D\right)$ cubic (ΔC_v^3) and quartic (ΔC_v^4) anharmonic contributions to the molar heat at constant volume are listed and compared with the values $\Delta C_v^{3,4} k - T(\partial^2 F_{3,4} / \partial T^2)_v$ obtained by help of the Feldman and Horton approximation [14] for the Mie—Lennard—Jones and Morse self-consistent potentials in Table IV.

Table II

Quasi-harmonic (U_{qh}), cubic (U_3) and quartic (U_4) anharmonic contributions to the zero-point energy of the RGC using the Singh's and Neb's (S—N), renormalized Morse (M) [12] and (12—6) Mie—Lennard—Jones (M—L—J) [14] potentials. The zero static lattice energy Φ_0 is showed for comparison

Solids	Potential	Zero-point energy [kJ/mol]			
		U_{qh}	$-U_3$	U_4	Φ_0
Ne	S—N	0.520	0.0034	0.1094	1.9034
	M	0.503	0.014		1.9044
	M—L—J	0.473	0.017	0.1210	2.4883
Ar	S—N	0.575	0.0015	0.0225	7.5469
	M	0.620	0.0045		7.3364
	M—L—J	0.698	0.0053	0.0363	8.4892
Kr	S—N	0.656	0.0007	0.0157	11.2043
	M	0.462	0.0016		10.8139
	M—L—J	0.562	0.0021	0.0141	11.7487
Xe	S—N	0.616	0.0005	0.0085	14.2732
	M	0.423	0.0001		14.6257
	M—L—J	0.503	0.0001	0.0071	16.5567

Table III

Comparison of the experimental data [9—11] for the molar heat at constant volume C_v of the RGC with calculated in terms of the Singh and Neb (S—N), selfconsistent Morse (M) [12] and Mie-Lennard-Jones (M—L—J) potentials

Solid	T [K]	C_v [J/mol·K]			
		Experiment	S—N	M	M—L—J
Ne	8	2.4283	3.9804	3.7480	2.6686
	16	11.7858	7.9845	7.9919	9.4773
	24	17.1784	13.4341	13.0662	13.5925
Ar	10	3.2964	3.1362	4.1458	3.5914
	20	12.1218	13.0896	8.5950	12.0462
	40	19.9545	15.0810	20.2705	19.2290
	60	23.2222	18.0880	22.2754	20.7754
	70	25.7181	19.8994	22.6743	20.9500
Kr	10	5.9185	7.7716	4.5057	
	20	15.6612	15.1782	16.4822	15.6126
	40	21.9231	15.9204	21.5247	21.1495
	60	23.3760	18.6740	23.1084	22.2219
	80	25.5876	21.4103	23.5830	22.3715
	100	27.7751	22.6751	24.6162	22.1720
Xe	10		7.7867	3.5659	17.0841
	20		16.6790	17.9579	17.0841
	40		18.5728	22.8619	21.9974
	60		19.4523	23.6493	22.9451
	80		21.8499	23.8445	23.0948
	100		22.9585	23.8833	23.0199
	120		23.5680	23.8964	22.7955
	140		23.9206	23.8642	22.5711

Table IV

The high temperature cubic (ΔC_v^3) and quartic (ΔC_v^4) anharmonic contributions to the molar heat at constant volume calculated in terms of the Singh and Neb (S—N), renormalized Morse (M) and (12—6) Mie-Lennard-Jones (M—L—J) potentials

Solids	T [K]	$\Delta C_{v \text{ anh}}$ [J/mol·K]				
		ΔC_v^3			$-\Delta C_v^4$	
		S—N	M	M—L—J	S—N	M—L—J
Ne	16	4.180	1.945	4.350	3.975	12.770
	24	5.015	2.612	6.525	4.296	15.314
Ar	50	0.492	1.306	2.220	4.838	4.489
	60	0.812	1.885	2.663	5.840	5.387
	70	0.951	2.287	3.107	5.933	6.285
Kr	60	1.560	1.442	1.706	3.079	3.366
	80	2.080	2.032	2.274	4.105	3.927
	100	2.600	2.681	2.843	5.131	4.489
Xe	60	0.553	0.924	1.152	1.083	2.259
	80	0.737	1.279	1.536	1.445	3.012
	100	0.921	1.655	1.920	1.806	3.765
	120	1.105	2.055	2.304	2.167	4.518
	140	1.289	2.481	2.688	2.519	5.271

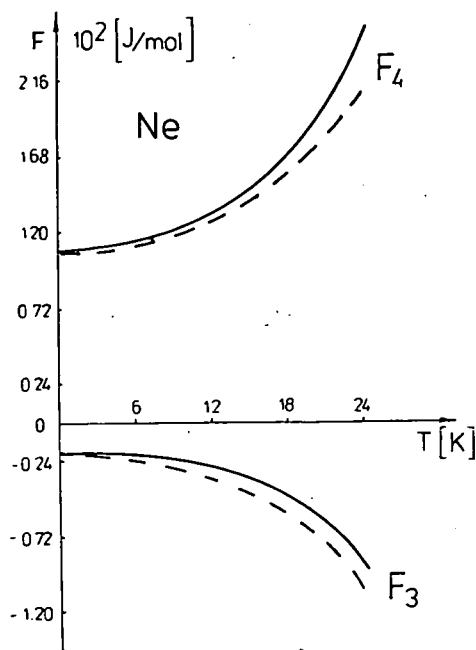


Fig. 1.a.

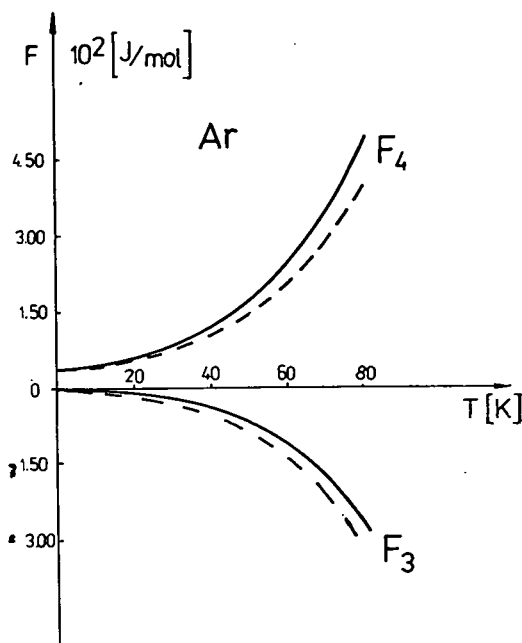


Fig. 1.b.

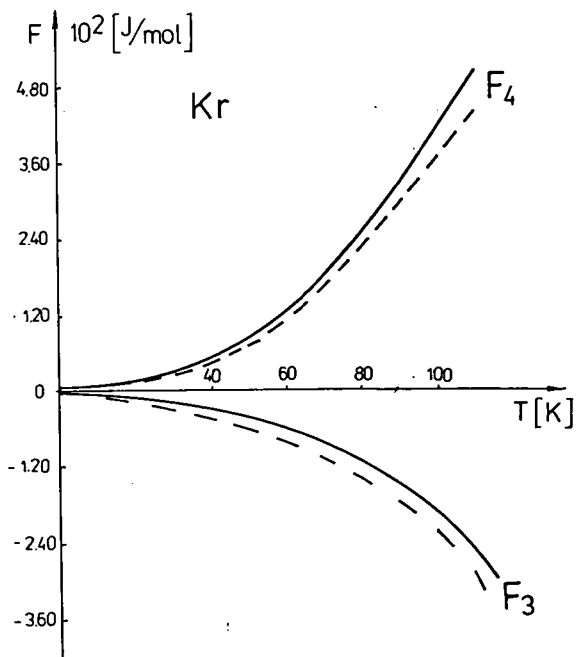


Fig. 1.c.

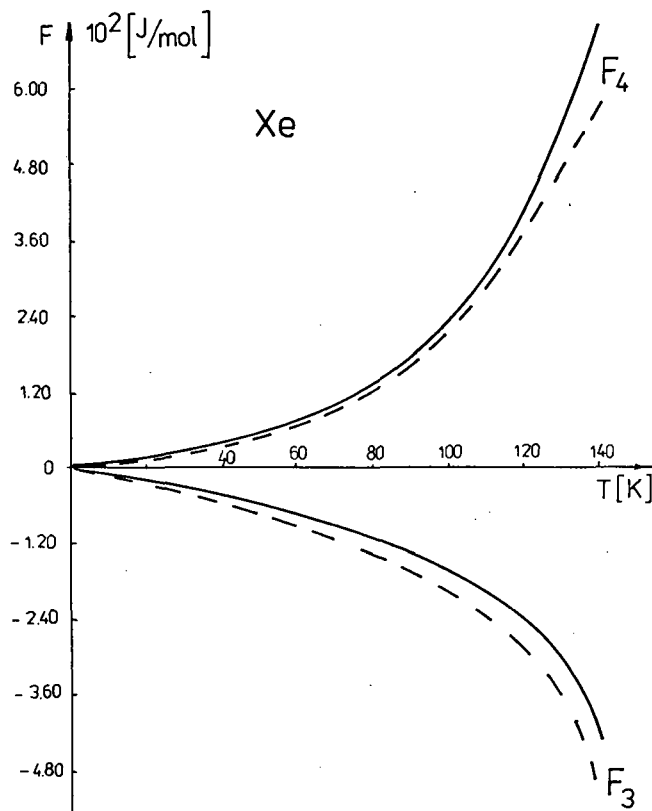


Fig. 1.d.

Figs. 1 (a, b, c, d). The cubic (F_3) and quartic (F_4) contributions to the free energy. Solid lines represent values obtained for Singh's and Neb's potential. The broken curves are evaluated for Mie-Lennard-Jones potential. (a) Ne; (b) Ar; (c) Kr; (d) Xe

The results calculated in terms of the S—N potential cubic (F_3) and quartic (F_4) contributions to the free energy (solid lines) as functions of temperature are shown and compared with those obtained for the M—L—J potential (dashed curves) in Figs. 1 (a, b, c, d) for all four solids. From Figs. 1 (a, b, c, d) we see that values F_3 and F_4 obtained in terms of the Singh and Neb model show the same temperature behaviour as has been found for the Mie-Lennard-Jones potential [13]. At higher temperature it is evident that allowance for thermal expansion has a large effect on the results obtained for Singh and Neb potential.

Summary and conclusions

With the approximation given in [7, 8] we have presented numerical calculations of predicted anharmonic contributions to vibrational thermodynamic properties of the inert-gas solids for Singh and Neb model potential (Tables II—IV). In these tables we have listed the thermodynamical quantities evaluated by help of the approximation made by other workers [13, 14, 17] with the Mie—Lennard—Jones [13, 14] and self-consistent Morse [12] potentials, for comparison. We have made a comparison with available experimental data in order to assess the validity of our potential model. Bearing in mind that a comparison of C_v values (Table III) is a demanding test it appears that the model is a reasonably realistic one for the RGC. A possible improvement in the description of anharmonic crystals is the investigation of effects of phonons in thermodynamic properties from the present model in the self-consistent theory which allows all higher-order terms of lower-order perturbation theory to be taken into account in a S. C. manner [18]. Work in this direction is in progress.

Appendix

The quantities FO , FQ , CH and UH appearing in Eqs. (2), (4), (5), (7) and (10)—(13) for the high and low temperature limits are equal to:

a) high temperature limit

$$FO = \ln 0.6505\beta + 0.04166\beta^2.$$

$$FQ = 0.1875\theta^2 + 0.0156\omega_L^2,$$

$$CH = \theta(0.125K - 0.0374G),$$

$$UX = 0.5CH - 0.04166\beta(0.125\omega_L K + 1/\theta),$$

$$\beta = \frac{\omega_L}{\theta}.$$

b) low temperature limit

$$FO = E_o - 0.2\pi^4\gamma,$$

$$FQ = 0.028E_o + 3.246\gamma,$$

$$CH = 0.125E_o(0.2997G - K)$$

$$UX = 0.0208E_o(0.0885G - K) - \omega_LE_o^{-1}(0.02177\omega_L K - 0.0231G).$$

Acknowledgement

The author gratefully thanks Professor L. WOJTCZAK, Head of the Department of Solid State Physics, University of Łódź, for helpful discussions connected with this paper and for reading the manuscript.

References

- [1] *Dobbs, E. R.*: Am. J. Phys. **28**, 243 (1960).
- [2] *Kittel, C.*: Introduction to Solid State Physics, PWN, Warsaw 1974 (in Polish).
- [3] *Pollack, G. K.*: Rev. Mod. Phys. **36**, (1964).
- [4] *Horton, G. K.*: Am. J. Phys. **36**, 93 (1968).
- [5] *Goodisman, J.*: Diatomic Interaction Potential Theory, Vol 1, Academic Press, New York—London, (1973).
- [6] *Singh, R. K., D. K. Neb.*: phys. stat. sol. (b) **112**, 735 (1982).
- [7] *Maradudin, A. A., P. A. Flin*: Ann. Phys. (USA) **15**, 337, 360 (1961).
- [8] *Flinn, P. A., A. A. Maradudin*: Ann. Phys. (USA) **22**, 223 (1963).
- [9] *Clusius, K., P. Flubacher, U. Piesbergen, K. Schleich, A. Sperandio*: Z. Naturforsch **15a**, 1 (1960).
- [10] *Flubacher, P., A. J. Leadbetter, J. A. Morrison*: Proc. Phys. Soc. **78**, 1449 (1961).
- [11] *Beaumont, R. H., H. Chihara, J. A. Morrison*: Proc. Phys. Soc. **78**, 1462 (1961).
- [12] *Malinowska-Adamska, C.*: Acta Phys. Hung. (1983) (in print).
- [13] *Leech, J. W., J. A. Reissland*: J. Phys. C3, 975, 987 (1970).
- [14] *Feldman, J. L., G. K. Horton*: Proc. Phys. Soc. **92**, 227 (1967).
- [15] *Reissland, J. A.*, Physics of Phonons, Izd. Mir, Moscow (1973) (in Russian).
- [16] *Hafemeister, D. W.*: J. Phys. Chem. Solids **30**, 117 (1969).
- [17] *Plakida, N. M., T. Siklós*: Acta Phys. Hung. **45**, 37 (1978).
- [18] *Plakida, N. M., T. Siklós*: phys. stat. sol **39**, 171 (1970).

ТЕРМОДИНАМИЧЕСКИЕ СВОЙСТВА КРИСТАЛЛОВ ИНЕРТНЫХ
ГАЗОВ С УЧЁТОМ КУБИЧЕСКИХ И ВЫСШИХ ПОРЯДКОВ
АНГАРМОНИЧЕСКИХ ВКЛАДОВ

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С использованием модельного потенциала Синга и Неба для парного центрального взаимодействия ближайших соседей исследуется температурная зависимость термодинамических функций кристаллов инертных газов в ангармоническом приближении.

Представлены результаты вычислений температурных зависимостей свободной и внутренней энергии, изохорной теплоёмкости с учётом кубических и высших порядков ангармонических вкладов в термодинамические функции для низких и высоких температур.

В частности, теоретические расчёты хорошо совпадают с экспериментальными данными для аргона, криптона и ксенона.