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## THERMODYNAMIC PROPERTIES OF SOLID NEON IN THE REDUCED ALL-NEIGHBOURS APPROXIMATION OF THE SELF-CONSISTENT PHONON THEORY

*The results of studies of physical properties of solid neon with the help of the reduced, all-neighbours approximation of the self-consistent phonon theory are presented. The interatomic interactions are described by the generalized Buckingham, Lennard-Jones and Morse self-consistent potentials. The parameters of these potentials in highest approximation with the number of nearest-neighbours are determined using experimental values for the lattice constant, cohesive energy, bulk modulus and the Debye characteristic temperature. Numerical results of our calculations for temperature and pressure dependence of selected physical properties are given and compared with available experimental data for Ne-20 fcc lattice.*

**Keywords:** self-consistent phonon theory, fcc atomic crystals, solid neon.

### 1. INTRODUCTION

The light rare gas atoms e.g. helium and neon with spherical symmetry crystallize in a cubic structure. The lattice atoms interact with mainly central forces [1] which have been represented by various models of pair potentials [2]. The traditional (12,6) Lennard-Jones potential, introduced originally for molecular crystals but usually used in any occasion, appeared too little effective

[3] because the  $r^{-12}$  repulsion term is not well founded theoretically from quantum mechanics [4]. Detailed considerations [3-5] lead to the power ( $r^{-6}$ ) and exponential laws, respectively, for the attraction and repulsion portion of the pairwise atomic interaction in these crystals. Thus, bearing in the mind all quantum mechanics considerations of physical properties for the heavier rare gas solids [6] and two isotopes of solid helium [7] we can state that the most common forms for interaction in these crystals are the  $(exp, m)$  Buckingham  $U_B(l)$ ,  $(exp, exp)$  Morse  $U_M(l)$  and the generalized  $(n, m)$  Lennard-Jones  $U_{LJ}(l)$  potential proposed by Shu Zhen and Davies [8]. The three mentioned potential models in simple harmonic approximation have the following analytical forms:

$$U_B(l) = C_B \left[ \frac{1}{\alpha} x_1 - \frac{1}{m} x_2^m \right], \quad (1)$$

$$U_M(l) = C_M \left[ \frac{1}{\alpha} x_1 - \frac{1}{\beta} x_3 \right], \quad \alpha > \beta, \quad (2)$$

$$U_{LJ}(l) = C_{LJ} \left[ \frac{1}{n} x_2^n - \frac{1}{m} x_2^m \right], \quad n > m, \quad (3)$$

where:  $C_B = \frac{\alpha m D_0}{\alpha - m}, \quad C_M = \frac{\alpha \beta D_0}{\alpha - \beta}, \quad C_{LJ} = \frac{n m D_0}{n - m},$   
 $x_1 = \exp[\alpha(1 - l/r_0)], \quad x_2 = r_0/l, \quad x_3 = \exp[\beta(1 - l/r_0)].$

In the above equations  $n$ ,  $m$ ,  $\alpha$  and  $\beta$  are the dimensionless parameters describing the slope of the potential curves,  $r_0$  and  $D_0$  define the potential minimum and are, respectively, the equilibrium distance of two isolated atoms and the energy of their dissociation. Numerical results of these parameters (Table 1), in higher approximation with respect to the number of nearest-neighbours, have been determined using experimental values for the zero-point volume, internal energy, the Debye characteristic temperature and the zero-point bulk modulus by the help of analytical results and method described in [7].

The pair potentials (1)-(3) are static ones and so they describe well only the harmonic crystal with very small atomic vibrations. In the case of high anharmonic crystal, as the solid neon, we have to replace them with their self-consistent versions, which take into account the higher-order anharmonic terms in the decompositions of the dynamic potential energy of crystal [9]. The version, called, the reduced all-neighbours approximation of the self-consistent phonon theory (RANASCPT) developed by us in [7] on the basis of thermodynamic double-time Green's function method [10] is applied here for calculations of physical properties of solid neon. It should be noted that in our earlier papers [11-13] we studied the lattice stability [11], thermodynamic [12]

and elastic properties [13] of solid neon in the reduced nearest-neighbours approximation of the self-consistent phonon theory, in which the simplifying assumption was taken that each atom interacts only with nearest-neighbours. Analysis of results reported in these cited papers shown that it is worth to take into account further shells of neighbours in the self-consistent equations describing the temperature  $T$  and pressure  $p$  variations of the dynamic and thermodynamic properties of anharmonic crystals. This improved theory is applied to the quantum crystal of the Ne-20.

## 2. THE BASIS OF THE SELF-CONSISTENT CALCULATIONS

The self-consistent method of incorporating atomic vibrations consists in replacing the pairwise static potentials  $U(l)$  (Eqs. (1)-(3)) with their dynamical self-consistent versions  $\tilde{\Phi}(l)$ , with  $l = l(T, p)$  [9].

Analytical expression for the  $\tilde{\Phi}(l)$  in terms of the  $(exp, m)$  Buckingham,  $(exp, exp)$  Morse and the  $(n, m)$  Lennard-Jones functions are derived in [7]. We shall not repeat here the equations given there but applying them to the fcc lattice of Ne-20 we will explore the temperature and pressure variations of its dynamic and thermodynamic properties in the RANASCPT.

Physical properties of solid neon are represented in this paper by the nearest neighbours separation  $l(l_i, z_i)$ , isothermal bulk modulus  $B_T(l_i, z_i)$ , the molar heat at constant pressure  $C_p(l_i, z_i)$  and the limiting temperature of dynamical stability  $T_s(l_i, z_i)$ , where  $l_i$  and  $z_i$  are, respectively, the radius and the filling of the  $i$ -th shell of neighbours.

Numerical calculations for all these quantities are performed on the basis of analytical results given for them in our previous papers [7, 14].

## 3. NUMERICAL RESULTS AND CONCLUSION

Applying the RANSCPT equations to the three mentioned above harmonic pair potentials (1-3) we have found for Ne-20 the optimal values of their parameters  $n$ ,  $\alpha$ ,  $\beta$ ,  $r_0$ ,  $D_0$  fitting them by trial-and-error method to the zero-point experimental data for the lattice constant, internal energy and isothermal bulk modulus. In these calculations, taking into account the van der Waals – London theory of molecular attraction, we have postulated  $m = 6$  in the  $(n, m)$  Lennard-Jones and  $(\alpha, m)$  Buckingham pair potentials. Simultaneously the repulsive

parameter  $\alpha = 14.10$  in the  $(\alpha, \beta)$  Morse pair potential was taken from the theoretical considerations of Hafemeister [4] based on the exchange charge model (ECM). All the parameters calculations were being carried out for various numbers  $i_{max}$  of shells of interacting neighbours – up to 20 shells – and the results are presented in Table 1.

Table 1

Optimal values of the generalised Lennard-Jones (LJ), Buckingham (B) and Morse (M) pair potential parameters for Ne-20 vs. the number  $i_{max}$  of shells of neighbours

	$i_{max}$	1	2	5	10	20
(n,m)LJ $m = 6$	$r_0$ [ $10^{-10}$ m]	2.98936	3.01090	3.04715	3.05445	3.05740
	$D_0$ [ $10^{-21}$ J]	0.77655	0.70100	0.59697	0.57859	0.57122
	$n$	18.67	17.48	16.27	16.10	16.04
$(\alpha, m)B$ $m = 6$	$r_0$ [ $10^{-10}$ m]	3.00115	3.02285	3.05826	3.06530	3.06819
	$D_0$ [ $10^{-21}$ J]	0.76392	0.69227	0.59448	0.57716	0.57023
	$\alpha$	18.88	18.08	17.31	17.20	17.17
$(\alpha, \beta)M$ $\beta = 14.1$	$r_0$ [ $10^{-10}$ m]	3.02490	3.04865	3.07136	3.07180	3.07180
	$D_0$ [ $10^{-21}$ J]	0.73814	0.68648	0.65115	0.65070	0.65070
	$\beta$	6.113	5.955	5.861	5.860	5.860

The above parameters were next used for detailed studies of the dynamic and thermodynamic properties of solid Ne. It's worth while to point out that Ne is the so called quantum crystal. Its atoms vibrate with high magnitudes even in the zero-point region and its structure becomes unstable below the Debye characteristic temperature and so up to the melting point Ne must be treated within the RANSCPT as a low temperature crystal against to the heavier RGS for which we consider both the low and high temperature region. At first, using the procedure described in our earlier paper [6], we have found the limiting temperatures of the dynamical stability of Ne for all sets of parameters (Table 2). Then, within the stability region, we were carrying out calculations of temperature and pressure variations of various physical quantities to test a validity of the theory we've applied.

In this paper we present only the temperature variations of nearest neighbours distance, isothermal bulk modulus and isobaric molar heat (Table 2 and Figures 1-3). It is because in the case of these quantities it is possible to compare theoretical results with experiment and, as it appeared earlier [6], in the nearest neighbours approximation of the SCPT (RSOSCPT) these quantities vary too rapidly at high temperatures and so it would be very interesting to check if taking into account further shells of neighbours improves the theoretical predictions.

Table 2

The nearest neighbours separation  $l(T = 20 \text{ K})$ , isothermal bulk modulus  $B_T(T = 20 \text{ K})$ , isobaric molar heat  $C_p(T = 20 \text{ K})$  and the limiting temperature of stability  $T_s$  as functions of the pair potential and the number of shells of neighbours. The experimental data [15] are given for comparison

	LJ		B		M		EXP
	1	20	1	20	1	20	
$l$ [ $10^{-10} \text{ m}$ ]	3.1904	3.1867	3.1929	3.1868	3.1939	3.1858	3.205
$B_T$ [GPa]	0.6422	0.6892	0.6150	0.6896	0.6330	0.7169	0.62
$C_p$ [J/mol·K]	24.005	22.862	27.676	24.610	32.268	26.251	18.90
$T_s$ ( $T_m$ ) [K]	26.8	27.2	25.9	26.7	26.0	27.0	(24.6)

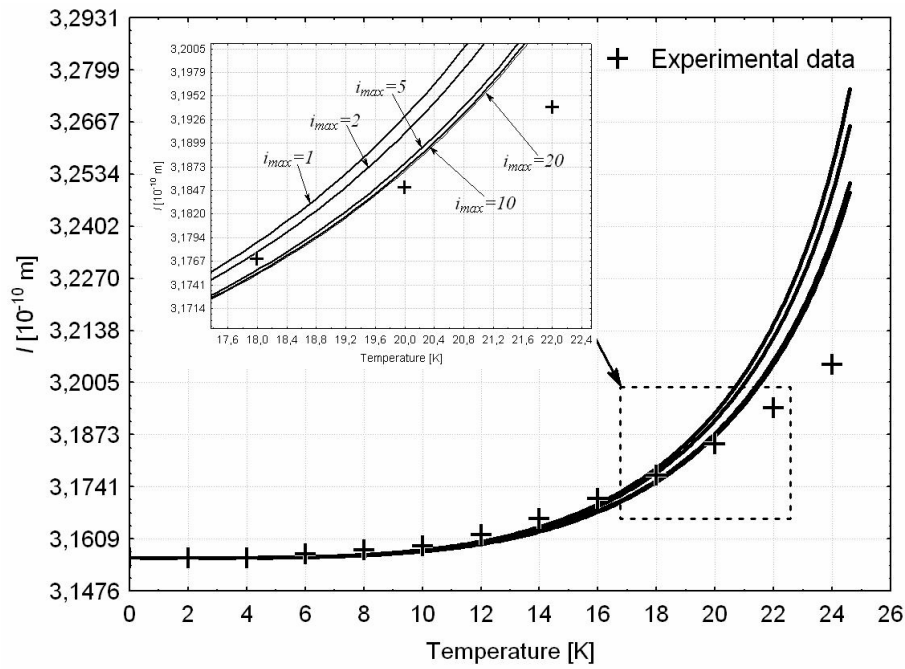


Fig. 1. Temperature variations of the nearest neighbours separation  $l$  in Ne-20 lattice obtained with the help of the Buckingham pair potential for various numbers of shells of interacting neighbours. Data for  $i_{\max} = 1$  correspond to the RSOSCT. The experimental data [15] are given for comparison

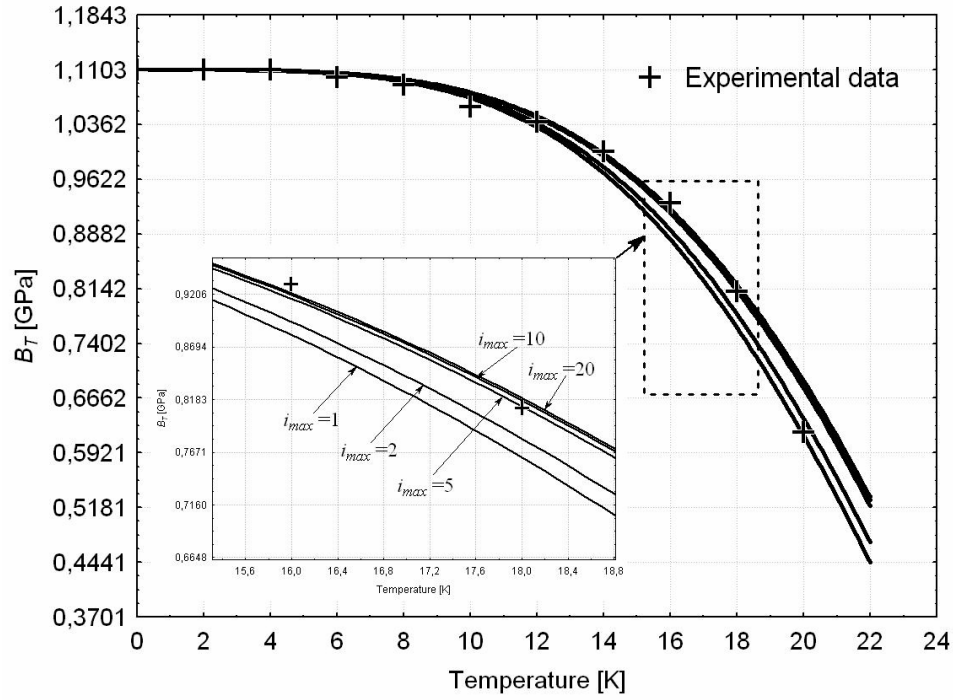


Fig. 2. Temperature variations of the isothermal bulk modulus  $B_T$  in Ne-20 lattice obtained with the help of the Buckingham pair potential for various numbers of shells of interacting neighbours. Data for  $i_{max} = 1$  correspond to the RSOSCPT. The experimental data [15] are given for comparison

From the collection of numerical results presented in Tables 1,2 and Figures 1,2,3 one can see, that all the quantities depend on the number of shells of interacting atoms taken in the RANSCT, however the results for  $i_{max} = 1$  and 10 differ very distinctly while these for  $i_{max} = 10$  and 20 are very close each other, and in the case of purely exponential Morse pair potential even equal, which indicates that these changes are convergent with respect to  $i_{max}$  and it is no use taking into account more than 20 shells of neighbours.

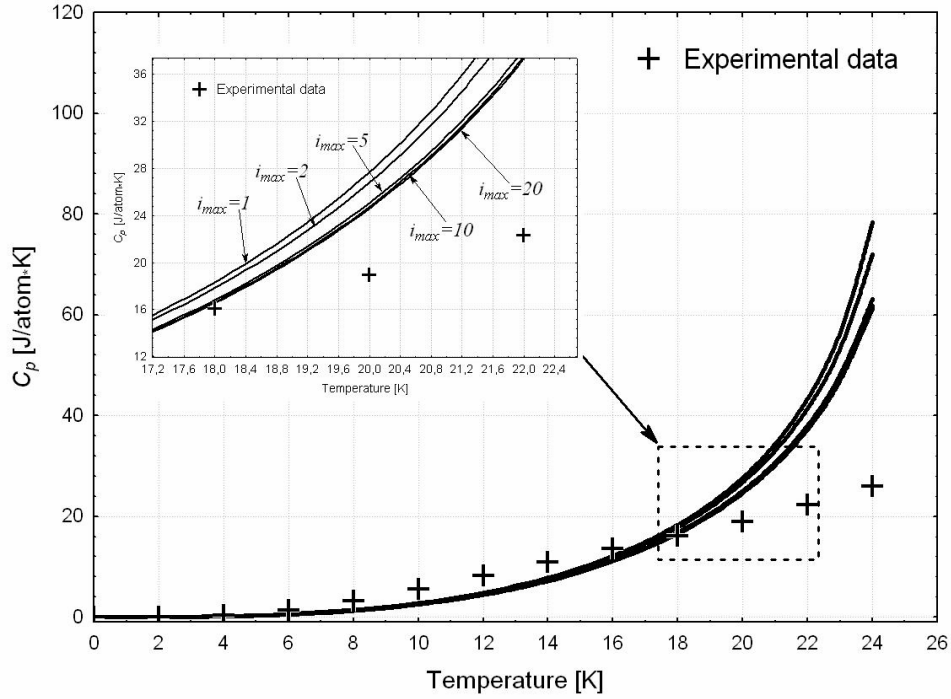


Fig. 3. Temperature variations of the isobaric molar heat  $C_p$  in Ne-20 lattice obtained with the help of the Buckingham pair potential for various numbers of shells of interacting neighbours. Data for  $i_{max} = 1$  correspond to the RSOSCPT. The experimental data [15] are given for comparison

If it about the potential parameters, we see that  $r_0$  is increasing while  $D_0$  and the slope parameters  $n$ ,  $\alpha$ ,  $\beta$  are decreasing with the rise in number of incorporated shells of neighbours. Additionally we can notice that the “all neighbours” Morse pair potential is dipper then the others (inversely than in the nearest neighbours approximation).

From the last column of Table 2 we see that the limit of dynamical stability  $T_s$  moves up and is still an upper estimation of the real melting point  $T_m$  so if we want to evaluate it more precisely we ought to analyse simultaneously both the solid and liquid phases with the help of their equations of state and the thermodynamic potentials.

If it about the nearest neighbours separation, isothermal bulk modulus and isobaric molar heat one can see that the theoretical predictions are generally getting better and better with a rise in number of shells of interacting atoms, that

is their nearest neighbours RSOSCPT too rapid high temperature changes are getting distinctly softer. However, we still see some discrepancies near the melting point and in the case of  $C_p$  even for medium temperatures. We suppose that these problems could be solved partly by taking into account more than four (as in the RSOSCPT and the RAN SCPT) terms in the potential energy decomposition in the crystal Hamiltonian. Besides let us mention that in the SCPT of Plakida and Siklós we use the two approximations, namely the low and high temperature limits and as for now there exists no transitional version. Whereas the surroundings of the melting point of solid Ne should be rather treated as medium than strictly low temperature region.

Summarising let us notice that no one of the three considered potential functions appeared distinctly better than the others so we should take them all for further studies at the improvement of the RANSCPT.

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**WŁAŚCIWOŚCI TERMODYNAMICZNE KRYSZTAŁU NEONU  
W APROKSYMACJI WSZYSTKICH SĄSIADÓW  
TEORII POLA SAMOUZGODNIONEGO**

**Streszczenie**

Praca zawiera wyniki badań właściwości termodynamicznych kryształu Ne-20. Obliczenia numeryczne wykonane są w przybliżeniu zredukowanym, drugiego rzędu teorii pola samouzgodnionego i uwzględniają wpływ dowolnej liczby powłok kolejnych sąsiadów na oddziaływania międzyatomowe w sieci. Oddziaływania te są aproksymowane 4-parametrowymi krzywymi  $(exp,m)$  Buckingham,  $(exp,exp)$  Morse i  $(n,m)$  Lennarda-Jonesa.

Szczegółowe wyniki obliczeń numerycznych, oparte na wyrażeniach analitycznych wyprowadzonych w pracach [7 i 14], otrzymane dla granicznej temperatury dynamicznej stabilności, odległości najbliższych sąsiadów, izotermicznego modułu ściśliwości oraz ciepła molowego przy stałym ciśnieniu zostały porównane z danymi doświadczalnymi [15].