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ORIGINAL ARTICLE

Thermodynamic functions of the hcp Coulomb crystal lattice

A.A. Kozhberov[1] · **D.A. Baiko**[1]

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Abstract One-component Coulomb crystals of ions with hexagonal close-packed (hcp) lattice likely form in the crust of strongly-magnetized neutron stars (magnetars). In this work we present a detailed study of vibration modes and thermodynamic properties of such crystals in a wide range of temperatures at zero magnetic field. In contrast to typically considered lattices, the phonon spectrum of the system exhibits a peculiar crossing of the acoustic modes near the Brillouin zone center in certain directions of the wavevector. It is demonstrated that in the field-free regime the Helmholtz free energy of the hcp Coulomb crystal is always higher than those of the Coulomb crystals with body-centered cubic and face-centered cubic lattices. The results of our numerical calculations are fitted by simple analytic expressions.

Keywords Neutron star · Dense matter · Coulomb crystal · Thermodynamics

1 Introduction

A system of positive point charges (ions) arranged in a crystal lattice and immersed into a uniform charge-compensating background of negative charge (electrons) is called a Coulomb crystal. This model is of primary importance for astrophysics. First of all, it is believed, that matter in white dwarf cores at later stages of star evolution crystallizes with a formation of Coulomb crystals. Moreover, neutron star envelopes in the density range spanning about 10 orders of magnitude, from $\sim 10^4$ g cm^{-3} to 10^{14} g cm^{-3}, are thought to be made of Coulomb crystals except the very early stages of the neutron star life.[1] Thus the knowledge of Coulomb crystal properties is necessary for interpretation of the observational data and for understanding the structure and evolution of these objects (e.g., Shapiro and Teukolsky 1983; Haensel et al. 2007; Baiko 2014).

Thermodynamic properties of Coulomb crystals have been studied in a number of works (e.g., Carr 1961; Pollock and Hansen 1973; Chabrier 1993; Potekhin and Chabrier 2010). Typically, only crystals with cubic symmetry are considered. For instance, in Baiko et al. (2001) (hereafter Paper I) the Helmholtz free energy was calculated and fitted with good accuracy for the body-centered cubic (bcc) and face-centered cubic (fcc) lattices using the harmonic lattice model. The bcc lattice has lower static binding energy and zero-point energy than the fcc lattice, however, the differences between the respective partial contributions to the total free energy are very small for these two lattices. Another lattice with very close static binding and zero-point energies is the hexagonal close-packed (hcp) lattice. The hcp lattice is similar to the fcc lattice in that both have the highest atomic packing factor among all lattices (for hard spheres). In Paper I an attempt was made to calculate the Helmholtz free energy of the hcp lattice as well, but an error was made in the general formula for the dynamic matrix. Consequently, the reported moments of the phonon spectrum and certain conclusions about the behavior of thermodynamic functions were not quite accurate.

✉ A.A. Kozhberov
kozhberov@gmail.com

[1] Ioffe Institute, Politekhnicheskaya 26, 194021 St. Petersburg, Russia

[1] Strictly speaking, in the inner neutron star crust, at densities above 4.3×10^{11} g cm^{-3}, the appearance of dripped neutrons may impact the ion dynamics (e.g., Chamel 2012).

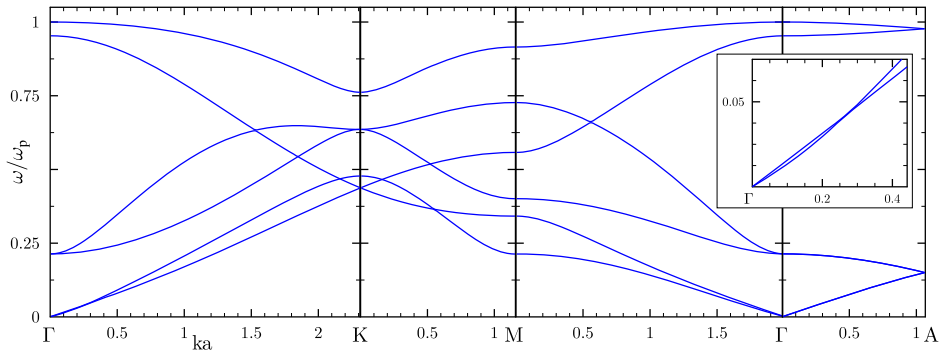

Fig. 1 Oscillation modes of the hcp lattice in certain high-symmetry directions

Neutron stars are also known to possess extremely high magnetic fields. An especially intriguing class of neutron stars is magnetars, in which the surface magnetic fields in the range of 10^{14}–10^{15} G have been detected (assuming the standard interpretation of neutron star braking due to magneto-dipole losses). It is not excluded that much higher magnetic fields are hidden in deeper layers of neutron star crust and core. Therefore, one also needs to know properties of magnetized Coulomb crystals, i.e. crystals in which the Lorentz force acting on an ion is comparable to the crystal restoring force.

Magnetized Coulomb crystals were considered for the first time qualitatively by Usov et al. (1980). Nagai and Fukuyama (1982) and (1983) have studied magnetized Coulomb crystals with bcc, fcc, and hcp lattices at zero temperature. Thermodynamics of magnetized Coulomb crystal at $T > 0$ has been constructed and fitted by analytic formulas in Baiko (2009), Baiko and Yakovlev (2013), but only for the bcc lattice. Nagai and Fukuyama (1983) have shown that the hcp lattice becomes thermodynamically preferable over the bcc lattice at $T = 0$ for certain orientations of the magnetic field with respect to the crystallographic axes provided the field is sufficiently strong. Clearly, this must also be the case for some range of finite temperatures. This has important consequences for the structure of magnetar crust, which may be of the hcp type in broad ranges of densities, temperatures and magnetic fields contrary to the typically assumed bcc crust structure.

To determine these ranges of physical parameters is not a straightforward task because very careful calculations are required to find thermal properties of the hcp lattice at low temperatures and strong magnetic fields. This will be the subject of our forthcoming work. In the present work we accomplish a necessary preliminary step and obtain thermodynamic properties of the hcp lattice at zero magnetic field. We improve and correct the previous computations of Paper I. Phonon spectra, phonon density of states, frequency moments and thermal properties are calculated with the relative accuracy of few parts in 10^4. The numerical results are fitted by simple analytic expressions.

2 Phonon spectrum and density of states

The frequency of ion oscillations around their lattice equilibrium positions ω can be found by solving the dispersion equation: $\det\{D_{ss'}^{\alpha\beta}(\mathbf{k}) - \omega_\nu^2(\mathbf{k})\delta^{\alpha\beta}\delta_{ss'}\} = 0$, where ν enumerates the oscillation modes ($\nu = 1, \ldots, 6$ for the hcp lattice) at given wavevector $\mathbf{k}$ in the first Brillouin zone, s and s' run over the ions in the elementary cell ($s, s' = 1, 2$), and $D_{ss'}^{\alpha\beta}(\mathbf{k}) = V_{ss'}^{\alpha\beta}(\mathbf{k}) + W_s^{\alpha\beta}\delta_{ss'}$ is the dynamic matrix. Practical formulas for the matrices $V_{ss'}^{\alpha\beta}(\mathbf{k})$ and $W_s^{\alpha\beta}$ can be found in Eqs. (4) and (5) of Kozhberov and Baiko (2012), where one has to make all ions in the lattice elementary cell identical. The familiar Kohn sum rule is satisfied for the squared phonon frequencies: $\sum_{\nu=1}^{6}\omega_\nu^2(\mathbf{k}) = 2\omega_\mathrm{p}^2$, where $\omega_\mathrm{p} = \sqrt{4\pi n Z^2 e^2/M}$ is the ion plasma frequency (Z is the ion charge number, M is the ion mass, and n is the ion number density).

Equations (4) and (5) of Kozhberov and Baiko (2012) for the dynamic matrix are suitable for any crystal in contrast to Eq. (3) of Paper I. In the latter work $W_s^{\alpha\beta}$ was assumed to be equal to $\omega_\mathrm{p}^2\delta^{\alpha\beta}/3$, which is true only for crystals with cubic symmetry, whereas for the hcp lattice, $W_s^{\alpha\beta} \neq \omega_\mathrm{p}^2\delta^{\alpha\beta}/3$. This mistake resulted in inaccurate values of phonon spectral moments and thermodynamic properties reported for this lattice. Note also, that in Nagai and Fukuyama (1983) the correct equation for $W_s^{\alpha\beta}$ was used.

The hcp lattice has two ions in the elementary cell and its phonon spectrum consists of six modes at each $\mathbf{k}$. Their frequencies are plotted in Fig. 1 in several high-symmetry directions as functions of the distance from the respective vertex of the irreducible part of the first Brillouin zone measured in units of the inverse ion sphere radius $1/a \equiv (4\pi n/3)^{1/3}$. Dispersion curves in Fig. 1 agree well with those shown in Fig. 3 of Nagai and Fukuyama (1983).

Near the center of the first Brillouin zone (vertex Γ), two modes are linear with respect to k (acoustic). However, in some directions (for instance, ΓK) this linear dependence is limited to a very narrow range of k near the Γ point. It is illustrated further in the inset in Fig. 1, where a crossing of the two acoustic modes is shown. The phonon modes of the

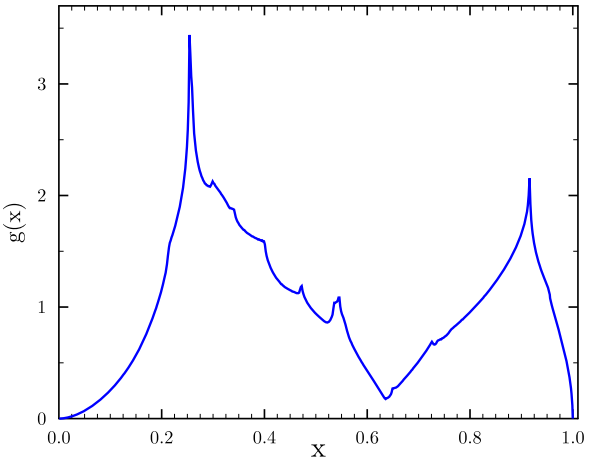

Fig. 2 Phonon density of states of the hcp lattice

bcc lattice do not have such a feature. This peculiar behavior is important for low temperature thermodynamics of the hcp lattice.

One of the main characteristics of the phonon spectrum is the phonon density of states

$$g(x) \equiv \frac{1}{3N} \sum_{\mathbf{k}\nu} \delta\big(x - \omega_\nu(\mathbf{k})/\omega_\mathrm{p}\big), \tag{1}$$

where N is the total number of ions, $x \equiv \omega/\omega_\mathrm{p}$, and the summation is over all wave vectors in the first Brillouin zone and over all phonon modes at each $\mathbf{k}$. The density of states is normalized so that $\int_0^1 g(x)\mathrm{d}x = 1$.

We have calculated the phonon density of states of the hcp lattice and it is shown in Fig. 2. At $x \ll 1$, $g(x) \approx 38x^2$. The quadratic dependence reflects the presence of acoustic phonons but in the hcp lattice it is limited to a rather narrow range of k due to the unusual behavior of the acoustic phonons shown in Fig. 1. The density of states has a square-root singularity at the upper boundary of the phonon spectrum and a number of square-root singularities at the Van Hove points (Van Hove 1953). These singularities are well known in the solid state physics and are associated with saddle points of the frequency spectrum (cf. also Kozhberov and Baiko 2014, where the bcc lattice density of states is discussed).

3 Phonon thermodynamics

In many applications the result is expressed as an average over the phonon spectrum of a function of the frequency, $f(\omega)$:

$$\big\langle f(\omega)\big\rangle = \frac{1}{3N} \sum_{\mathbf{k}\nu} f\big(\omega_\nu(\mathbf{k})\big). \tag{2}$$

Table 1 Moments of the hcp lattice

u_3	u_1	u_{-1}	u_{-2}	u_ln
0.24983	0.5133369	2.70183	11.8421	−0.816031

If the function is a simple power-law, this becomes the phonon-spectrum moment $u_n = \langle(\omega/\omega_\mathrm{p})^n\rangle$. Also of interest is the average logarithm of the frequency $u_\mathrm{ln} = \langle\ln(\omega/\omega_\mathrm{p})\rangle$. Averages of more complex functions are necessary to compute phonon thermodynamic potentials. In particular, thermal phonon contributions to the Helmholtz free energy, energy, and heat capacity read

$$\begin{aligned} F &= 3NT\big\langle\ln\big(1-\mathrm{e}^{-w}\big)\big\rangle \equiv NTf^\mathrm{th}(t), \\ E &= 3NT\left\langle\frac{w}{e^w-1}\right\rangle, \\ C &= 3N\left\langle\frac{w^2}{4\sinh^2(w/2)}\right\rangle, \end{aligned} \tag{3}$$

respectively, where $w = x/t$, $t = T/T_\mathrm{p}$, and $T_\mathrm{p} \equiv \hbar\omega_\mathrm{p}$ is the ion plasma temperature ($k_\mathrm{B} = 1$). In principle, it is possible to calculate such averages as one-dimensional integrals with the phonon density of states: $\langle f(\omega)\rangle = \int_0^1 \mathrm{d}x g(x) f(x)$. However, we prefer Holas method of three-dimensional integration over the first Brillouin zone combined with modified Gaussian quadrature rule (Holas 1977; Albers and Gubernatis 1981).

Our results for the spectral moments are presented in Table 1. The same value for u_1 has been reported previously (Nagai and Fukuyama 1982). In Paper I, only four significant figures of this moment were found correctly. Calculations of the other moments of the hcp lattice in Paper I were not accurate enough (there was a 1.5 % error in the u_{-2} value and $\leq$0.1 % errors in values of the other moments). Note, that Madelung constants and moments for bcc and fcc lattices reported in Paper I were correct as well as the Madelung constant for the hcp lattice.

In Fig. 3 we present our results for thermal phonon contributions to the thermodynamic functions of the hcp lattice. We show ratios of F, E, and C of the hcp lattice to the same quantities of the bcc and fcc lattices as functions of t. One can easily appreciate the difference between the lattices at low (quantum) and intermediate temperatures. In particular, in the quantum limit $T \ll T_\mathrm{p}$, $F_\mathrm{hcp}/F_\mathrm{bcc} = E_\mathrm{hcp}/E_\mathrm{bcc} = C_\mathrm{hcp}/C_\mathrm{bcc} \approx 1.190$, and $F_\mathrm{hcp}/F_\mathrm{fcc} = E_\mathrm{hcp}/E_\mathrm{fcc} = C_\mathrm{hcp}/C_\mathrm{fcc} \approx 1.089$.

It is also clear that the thermodynamic functions of the hcp lattice approach the Debye limit ($C \propto T^3$, $F, E \propto T^4$) at much lower temperatures than those of the bcc and fcc lattices. One can see, that $C_\mathrm{fcc}/C_\mathrm{bcc}$ saturates in the quantum limit at higher temperature than $C_\mathrm{hcp}/C_\mathrm{bcc}$ and $C_\mathrm{hcp}/C_\mathrm{fcc}$.

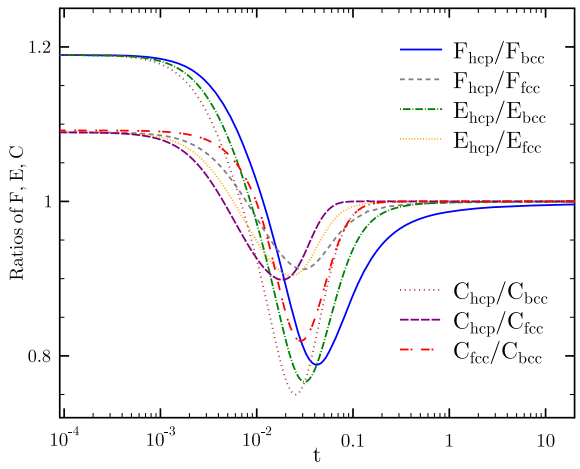

Fig. 3 Ratios of thermal free energy, thermal energy and heat capacity of bcc, fcc, and hcp lattices

More quantitatively, the Debye T^3-law for the heat capacity is satisfied with accuracy of less than half a percent at $T \approx 10^{-3}\,T_\mathrm{p}$ for the hcp lattice, and at almost an order of magnitude higher temperature, $T \approx 9\times10^{-3}T_\mathrm{p}$, for the bcc lattice. The difference can be traced back to the peculiar properties of the hcp lattice acoustic modes near the Brillouin zone center, cf. Fig. 1.

At intermediate temperatures all the ratios have minima. The hcp to bcc ratios $F_\mathrm{hcp}/F_\mathrm{bcc}$, $E_\mathrm{hcp}/E_\mathrm{bcc}$, and $C_\mathrm{hcp}/C_\mathrm{bcc}$ reach ≈0.789, 0.765, and 0.75 at $t \approx 0.042$, 0.03, and 0.025. The hcp to fcc ratios have the respective minima of 0.912, 0.904, and 0.9 at $t \approx 0.031$, 0.022, and 0.018. At high temperatures, all the ratios approach 1 as a consequence of the Dulong-Petit law. The thermal free energy in this limit behaves as $F_\mathrm{hcp} = 3NT[\ln(1/t)+u_\mathrm{ln}] - 1.5N\hbar\omega_\mathrm{p}u_1$. (For the hcp lattice, the asymptote is valid with deviation of less than half a percent at $t > 1.43$.) Due to the logarithmic temperature dependence and the presence of lattice specific spectral moments in the free energy asymptote, the ratios of free energies converge to 1 slower than the ratios of energies and heat capacities.

It is possible to approximate the temperature dependence of F, E, and C for the hcp lattice by simple analytic formulas. Since all these quantities for the bcc lattice are already calculated and fitted in Paper I, it turned out to be the easiest to approximate the ratios shown in Fig. 3:

$$\frac{F_\mathrm{hcp}}{F_\mathrm{bcc}} = \frac{a_1 + a_2t^{a_3} + a_4(1+a_5\exp(-a_6t))t^{a_7}}{a_8 + a_9t^{a_{10}} + a_4(1+a_{11}\exp(-a_{12}t))t^{a_7}}, \tag{4}$$

$$\frac{E_\mathrm{hcp}}{E_\mathrm{bcc}} = \frac{b_1 + b_2t^{b_3} + b_4(1+b_5\exp(-b_6t))t^{b_7}}{b_8 + b_9t^{b_{10}} + b_4(1+b_{11}\exp(-b_{12}t))t^{b_7}}, \tag{5}$$

$$\frac{C_\mathrm{hcp}}{C_\mathrm{bcc}} = \frac{c_1 + c_2t^{c_3} + c_4(1+c_5\exp(-c_6t))t^{c_7}}{c_8 + c_9t^{c_{10}} + c_4(1+c_{11}\exp(-c_{12}t))t^{c_7}}. \tag{6}$$

These approximations have a fractional accuracy ≈10^{-4}, while calculations were performed with an accuracy of five significant digits for t from 10^{-5} to 10^3. The fitting coefficients a_i, b_i, and c_i are given in Table 2.

Table 2 Fitting parameters a_i, b_i and c_i

i	a_i	b_i	c_i
1	0.00011896	1.1896×10^{-6}	1.1896×10^{-6}
2	−0.25073	0.0013725	0.003519
3	2.946	1.471	1.5812
4	34.409	0.71255	1575
5	3.1134	−3.17712	−0.085359
6	87.731	38.823	22.897
7	3.1488	3.2672	5.0573
8	0.0001	10^{-6}	10^{-6}
9	0.20664	0.00224	0.0053389
10	1.8819	1.5457	1.6404
11	0.10895	−3.233	1.5672
12	19.352	43.925	53.545

Table 3 ζ and u_1 for bcc, fcc, and hcp lattices

	bcc	fcc	hcp
ζ	−0.8959292557	−0.8958736152	−0.8958381205
u_1	0.5113877	0.513194	0.5133369

We are now in a position to compare the total Helmholtz free energies of the bcc, fcc, and hcp lattices at any temperature (below melting), ion density, charge and mass. In harmonic approximation and neglecting the electron background polarizability effect, the free energy consists of the static binding, the zero-point, and the thermal phonon contributions:

$$\frac{F^\mathrm{tot}}{NT} = \zeta\Gamma + 1.5u_1/t + f^\mathrm{th}(t). \tag{7}$$

In this case, ζ is the Madelung constant and $\Gamma = Z^2e^2/(aT)$ is the Coulomb coupling parameter. For reference, the values of ζ and u_1 for the three lattices are summarized in Table 3.

Consider the difference of F^tot between the three lattices. At any t and $\Gamma > 175$ (which corresponds to the crystal phase), $(\zeta_\mathrm{hcp}-\zeta_\mathrm{fcc})\Gamma + 1.5(u_\mathrm{1hcp}-u_\mathrm{1fcc})/t > 0$ and $(\zeta_\mathrm{fcc}-\zeta_\mathrm{bcc})\Gamma + 1.5(u_\mathrm{1fcc}-u_\mathrm{1bcc})/t > 0$, while at low temperatures ($t \lesssim 0.007$), $f^\mathrm{th}_\mathrm{hcp} < f^\mathrm{th}_\mathrm{fcc} < f^\mathrm{th}_\mathrm{bcc}$ (cf. Fig. 3, $f^\mathrm{th} < 0$). Nevertheless, at these low temperatures the thermal phonon contribution is much smaller than the zero-point one. For instance, one can see in Fig. 3 that $f^\mathrm{th}_\mathrm{hcp} = f^\mathrm{th}_\mathrm{fcc}$ at $t \approx 0.0078$. At this t, $1.5(u_\mathrm{1hcp}-u_\mathrm{1fcc})/t = 0.02748$ and it increases with decrease of temperature. But $f^\mathrm{th}_\mathrm{hcp} - f^\mathrm{th}_\mathrm{fcc}$ reaches a minimum of $\approx -1.044\times10^{-6}$ at $t = 0.0057$. It is, therefore, impossible to compensate the difference of the static-binding and zero-point energies by the difference of the thermal contributions

at any Γ and t. Since these two parameters fully determine thermodynamics of a Coulomb crystal, we conclude that for any T, n, Z, and M, $F^{\rm tot}_{\rm bcc} < F^{\rm tot}_{\rm fcc} < F^{\rm tot}_{\rm hcp}$. This means, that under the assumptions stated above, in non-magnetized matter, formation of the bcc lattice is always thermodynamically preferred.

4 Conclusions

It follows from the results of Nagai and Fukuyama (1983) that formation of Coulomb crystals of ions with the hexagonal close-packed lattice may be expected in highly-magnetized neutron star crust, which underlines the importance of this system for astrophysics. We have studied phonon modes and have improved and corrected previous calculations (Paper I) of spectral moments and thermodynamic functions of this lattice using harmonic approximation. The phonon spectrum of the hcp lattice displays a peculiar behavior near the center of the first Brillouin zone, where two acoustic modes have a crossing for certain directions of the phonon wavevector. This feature is absent in other typically considered Coulomb lattices, and it affects noticeably thermodynamic properties of the hcp lattice at low temperatures. The phonon heat capacity of the hcp lattice at low temperatures is found to be 1.2 times bigger than that of the bcc lattice. It is shown, that at any temperature, mass density, ion charge, and ion mass, the total Helmholtz free energy of the bcc lattice is below that of the fcc lattice, which, in turn, is below that of the hcp lattice (neglecting anharmonicity and electron polarization effects). The ratios of phonon free energies, energies, and heat capacities of the hcp and bcc lattices are fitted by simple analytic expressions. The phonon density of states of the hcp lattice is also calculated.

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