

Electrostatic properties and stability of Coulomb crystals

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Abstract

We calculate the electrostatic properties of more than 20 different Coulomb crystals and study their resistance to small oscillations of the ions around their equilibrium positions (phonon oscillations). We discuss the stability of multi-component crystals against separation into set of one-component lattices and for some cases, the influence of energy of the zero-point vibrations. It is confirmed that the body-centred cubic (bcc) lattice possesses the lowest electrostatic energy among all one-component (one type of ion in the elementary cell) crystals. For systems composed of two types of ions (their charge and density numbers are Z_1, n_1 and Z_2, n_2 , respectively) and for $n_1 = n_2$, it is found that the formation of a binary bcc lattice is possible at $1/2.4229 < \alpha < 2.4229$, where $\alpha \equiv Z_2/Z_1$. Under the same conditions, the NaCl lattice forms at $\alpha > 5.197$ and $\alpha < 0.192$. While for $n_2 = 2n_1$, the MgB_2 lattice is found be stable at $0.1 < \alpha < 0.32$. For multicomponent lattices with hexagonal structure (binary hexagonal close-packed, MgB_2 and some others lattices), it is shown that their properties depend on the distance between hexagonal layers and this distance changes with α .

KEYWORDS

coulomb crystals, electrostatic energy, stability

1 | INTRODUCTION

A Coulomb crystal is a system of point-like charges (hereafter, ions) arranged in a crystal lattice and immersed into a neutralizing background of opposite charges (hereafter, electrons), which in turn is usually considered as uniform. This model is in use in various branches of physics, including solid state theory and theory of dusty plasmas,^{1–3} but the greatest advancement it achieves in the theory of degenerate stars, where Coulomb crystals help to describe the neutron stars crust and envelopes of old white dwarfs.^{4,5}

In this paper, we study various Coulomb crystals, which differ in the type of crystal lattice and in composition. Crystals in which all ions have the same charge Ze , we call one-component, binary crystals have two different ions in the elementary cell, while crystals with three different ions are called three-component. The type of lattice that is formed in the current situation is determined by the minimum of electrostatic energy (it is also called a Madelung energy). It is known that the body-centred cubic (bcc) lattice has the lowest electrostatic energy^{6–10} while for multicomponent lattices, complex analysis is mainly absent.

In the context of the neutron stars crust theory, which is the main point of our interest, multi-component crystals, both in the Coulomb approximation and in a more detailed approach, were investigated in several works. Crystal structures of He-C-O, C-O-Ne, and C-O-Fe mixtures were examined in Ref.¹¹ where it was shown that multicomponent crystals can form between layers of one-component bcc crystals. A similar result was obtained in Ref.¹² where the issue of the

formation of multicomponent crystals in the outer crust of a cold nonaccreting neutron star was considered. In Ref.¹² possibilities of the formation of multicomponent crystal mixtures in the outer crust of a cold nonaccreting neutron star were studied. From a comparison of the Gibbs free energies at a fixed pressure and $T = 0$ (the difference comes from the electrostatic energy, while the energy of zero-point vibrations and the electron background polarization effect is not taken into account), it was shown that between the one-component ^{56}Fe and ^{62}Ni layers formation of a binary bcc lattice of these ions is possible, and the same happens between ^{80}Ni and ^{124}Mo ion layers. For the accreted neutron star crust, the number of possible compounds with the binary bcc lattice structure is much larger.¹³

In this paper, we follow the basic ideas of Refs.^{11,12} We use the analytical expression evaluated in Refs.^{14,15} to calculate the electrostatic energies of various lattices, including those that were never studied before. For some lattices, we study their resistance to small ion oscillations around the equilibrium positions (phonon oscillations) and the stability of multicomponent crystals against separation into a set of one-component lattices. The energy of zero-point vibrations of several lattices and its effect on the total energy are also briefly discussed.

2 | NOTATIONS

Consider a multicomponent Coulomb crystal with N_{cell} ions in its elementary cell. The potential energy of this crystal is given by

$$U = \frac{1}{2} \sum_{lp'l'} (1 - \delta_{pp'} \delta_{ll'}) \frac{Z_p Z_{p'} e^2}{|\mathbf{r}_{lp} - \mathbf{r}_{l'p'}|} - n_e \sum_{lp} \int d\mathbf{r} \frac{Z_p e^2}{|\mathbf{r}_{lp} - \mathbf{r}|} + \frac{1}{2} n_e^2 e^2 \int \int \frac{d\mathbf{r} d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|},$$

where n_e is the electron number density, the radius vector of p -ion with charge number Z_p is equal $\mathbf{r}_{lp} = \mathbf{X}_{lp} + \mathbf{u}_{lp}$, \mathbf{u}_{lp} is the ion displacement from its equilibrium position \mathbf{X}_{lp} . The indices p and p' numerate the ions in the elementary cell ($p = 1, \dots, N_{\text{cell}}$). Hereinafter, the thermodynamic limit is used. This means that the number of ions N and the volume V tend to infinity while the ion number density n is fixed (for mixtures n is the ion number density of all ions). Hence, sums over l and l' are extended to infinity.

In a crystal, motions of ions can be considered as small oscillations around the equilibrium positions, and their potential energy can be expanded in powers of \mathbf{u}_{lp} ,

$$U \approx U_M + \frac{1}{2} \sum_{lp'l'} u_{lp}^\mu u_{l'p'}^\lambda \frac{\partial^2 U}{\partial u_{lp}^\mu \partial u_{l'p'}^\lambda}, \quad (1)$$

where Greek indices μ and λ enumerate Cartesian components of the vector, the Madelung (electrostatic) energy U_M is the energy of the crystal when all its ions are fixed at their equilibrium positions. Equilibrium positions of ions are given by vector $\mathbf{X}_{lp} = \mathbf{R}_l + \chi_p$, where $\mathbf{R}_l = l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2 + l_3 \mathbf{a}_3$ is a lattice vector, l_1, l_2, l_3 are arbitrary integers, vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ are lattice main translation vectors, χ_p is the basis vector of the p -ion in the elementary cell (by construction we always have $\chi_1 = 0, \chi_p \neq 0$ for $p > 1$). For a simple cubic (sc) lattice $\mathbf{a}_1 = a_1(1, 0, 0)$, $\mathbf{a}_2 = a_1(0, 1, 0)$ and $\mathbf{a}_3 = a_1(0, 0, 1)$, where a_1 is the lattice constant.

In Refs.^{14,15} a practical formula of the Madelung energy of any ordered multicomponent Coulomb crystal was derived:

$$U_M = N \frac{Z_1^2 e^2}{a} \xi, \quad \xi = \frac{a}{2N_{\text{cell}}} \sum_{lp'l'} \frac{Z_p Z_{p'}}{Z_1^2} (1 - \delta_{pp'} \delta_{\mathbf{R}_l, 0}) \frac{\text{erfc}(AY_{lp'l'})}{Y_{lp'l'}} - \frac{Aa}{N_{\text{cell}} \sqrt{\pi}} \sum_p \frac{Z_p^2}{Z_1^2} - \frac{3}{8N_{\text{cell}}^2 A^2 a^2} \sum_{pp'} \frac{Z_p Z_{p'}}{Z_1^2} + \frac{3}{2N_{\text{cell}}^2 a^2} \sum_{mp'l'} \frac{Z_p Z_{p'}}{Z_1^2} (1 - \delta_{\mathbf{G}_m, 0}) \frac{1}{G_m^2} \exp \left[-\frac{G_m^2}{4A^2} + i\mathbf{G}_m(\chi_p - \chi_{p'}) \right]. \quad (2)$$

In this case, $\mathbf{Y}_{lp'l'} = \mathbf{R}_l + \chi_p - \chi_{p'}$, $\text{erfc}(x)$ is a complementary error function, and $a \equiv (4\pi n/3)^{-1/3}$ is the ion sphere radius. Vectors $\mathbf{G}_m = m_1 \mathbf{g}_1 + m_2 \mathbf{g}_2 + m_3 \mathbf{g}_3$ form a reciprocal lattice, where $\mathbf{g}_1, \mathbf{g}_2, \mathbf{g}_3$ are the main translation vectors of the reciprocal lattice, and m_1, m_2, m_3 are arbitrary integers. An arbitrary parameter A is chosen so that sums \mathbf{R}_l and \mathbf{G}_m ,

converge equally rapidly. The parameter ξ is called a Madelung constant. It depends only on the type of lattice and charge numbers of ions.

3 | ONE-COMPONENT LATTICES

Madelung constants of one-component ($Z_p = Z_1$) lattices were studied in a large number of works.^{6–10} Usually, authors restrict themselves to considering sc, bcc, face-centred cubic (fcc), and hexagonal close-packed (hcp) lattices. In 1978, Foldy calculated the Madelung constant of the diamond lattice.¹⁶ In 1991, Zucker did the same for fluorite, perovskite, and spinel,¹⁷ but he made a mistake: ξ for the perovskite lattice was less than -0.9 . Although it is known that the electrostatic energy of a Coulomb crystal in the Wigner-Seitz approximation is $-0.9(Ze)^2/a^4$ and this is the lower limit for this energy.¹⁸ Therefore, the Madelung constant of any lattice should be greater than -0.9 . Zucker's mistake was fixed in Ref.¹⁹

Nowadays the electrostatic energies of eight one-component lattices are known. Most accurate electrostatic energies of the bcc and fcc lattices were computed in Ref.²⁰ (12 significant digits versus seven in Ref.⁸):

$$\xi_{\text{bcc}} = -0.895929255682, \quad (3)$$

$$\xi_{\text{fcc}} = -0.895873615195. \quad (4)$$

It absolutely agrees with our calculations. Other Madelung constants are known with less accuracy. In the present work, we recalculated all of them (excluding the spinel lattice, its Madelung constant is -0.8492675^{17}).

The Madelung constant of the sc lattice is $\xi_{\text{sc}} = -0.88005944211$.¹⁴

Fluorite is a mineral form of CaF_2 . Its crystal lattice can be described as a sc lattice with twelve basis vectors: $\chi_1 = 0$, $\chi_2 = 0.5a_1(1, 1, 0)$, $\chi_3 = 0.5a_1(0, 1, 1)$, $\chi_4 = 0.5a_1(1, 0, 1)$, $\chi_{5-12} = 0.25a_1(\pm 1, \pm 1, \pm 1)$. For this lattice, $na_1^3 = 12$ (for any lattice with cubic symmetry $na_1^3 = N_{\text{cell}}$) and $\xi_{\text{CaF}_2} = -0.86445318436682$.

Perovskite is a calcium titanate mineral (CaTiO_3). Its crystal lattice can be described as a sc lattice with five basis vectors: $\chi_1 = 0$, $\chi_2 = 0.5a_1(1, 0, 0)$, $\chi_3 = 0.5a_1(0, 1, 0)$, $\chi_4 = 0.5a_1(0, 0, 1)$, $\chi_5 = 0.5a_1(1, 1, 1)$. For a one-component perovskite lattice $\xi_{\text{CaTiO}_3} = -0.8473240413727$. Note that in Ref.²¹ it was suggested that ions in the inner crust of a neutron star form one-component perovskite crystals but this statement was not proofed in Refs.^{11,12} and seems to us is incorrect.

We describe the diamond crystal lattice (diam) as a sc lattice with eight basis vectors: $\chi_1 = 0$, $\chi_2 = 0.5a_1(1, 1, 0)$, $\chi_3 = 0.5a_1(0, 1, 1)$, $\chi_4 = 0.5a_1(1, 0, 1)$, $\chi_5 = 0.25a_1(1, 1, 1)$, $\chi_6 = 0.25a_1(-1, -1, 1)$, $\chi_7 = 0.25a_1(1, -1, -1)$, and $\chi_8 = 0.25a_1(-1, 1, -1)$. Madelung constant of the diamond lattice is -0.83542570276483 .

The hcp lattice should be discussed in detail. A hcp lattice is a hexagonal lattice (the main translation vectors are used: $\mathbf{a}_1 = a_1(1, 0, 0)$, $\mathbf{a}_2 = 0.5a_1(1, \sqrt{3}, 0)$, $\mathbf{a}_3 = a_1(0, 0, h)$) with two basis vectors: $\chi_1 = 0$ and $\chi_2 = 0.5a_1(1, 1/\sqrt{3}, h)$, where h is the height of the elementary cell. In an ordinary hcp lattice the height is taken to be equal $h_0 = \sqrt{8/3} \approx 1.632993$, which follows from the problem of close-packing of equal spheres. However, the electrostatic energy of the hcp Coulomb lattice reaches a minimum at $h = h_{\text{min}} \approx 1.635639 \neq h_0$. At such height, $\xi_{\text{hcp}}^{\text{min}} = -0.895838451$ in contrast to the traditionally accepted value $\xi_{\text{hcp}} = -0.895838120459$ at $h = h_0$.²⁰ Previous investigations of the minimum of the hcp electrostatic energy were performed by Nagai and Fukuyama.²² They obtained $h_{\text{min}} \approx 1.633$ and suggested that $h_{\text{min}} = \sqrt{8/3}$. Fortunately, this distinction is not significant.²³

The hcp lattice with arbitrary h we call a ‘‘hexagonal packed’’ (hp) lattice. For h between 1.48 and 1.82 ξ_{hp} could be fitted as

$$\xi_{\text{hp}} = -0.7922842 - 0.1130638h + 0.02212615h^2 + 0.00506955h^3. \quad (5)$$

At $h \approx 2.727$ the hp lattice turns to the terrestrial α -graphite lattice with the Madelung constant -0.840878927 .

Similarly, in the hexagonal (hex) lattice (hcp lattice without χ_2) the distance between the hexagonal layers can be arbitrary. The electrostatic energy of the hex lattice is minimal at $h = h_{\text{hex0}} = 0.928$, when the Madelung constant is $\xi_{\text{hex0}} = -0.887321284742$. For $h = h_{\text{hex}} = \sqrt{8/3}$, the Madelung constant of the hex lattice is $\xi_{\text{hex}} = -0.77943336427$.¹⁴

Note that in the current paper, we do not discuss deformed bcc and fcc lattices. It is widely done in Refs.^{24,25} where it was found that no deformation can bring the bcc lattice to a state with a lower electrostatic energy. Thus, the bcc Coulomb lattice has the lowest electrostatic energy among all lattices under consideration.

It should be mentioned a few words about the effects of the electron background polarization on electrostatic energy. For the first time in the context of the theory of degenerated stars, they were studied in Ref.²⁶ where the Thomas-Fermi (TF) linear response formalism and the Jancovici (J) random phase approximation were used to define the dielectric function.

In Ref.²³ it was shown that the model of a Coulomb crystal with a polarized electron background, described by TF formalism, is similar to the model of a dusty Yukawa crystal with a nondegenerate background, which was widely discussed in Refs.^{27–30} The electrostatic energy in both models is described by the same analytical equation and is as yet calculated for one-component bcc, fcc, hcp, and MgB₂ lattices.²³ Note that among these four lattices, the bcc lattice possesses the lowest electrostatic energy at $\kappa\alpha < 1.065714$, while at higher $\kappa\alpha$ the fcc lattice has the lowest U_M , where $\kappa \equiv \sqrt{4\pi e^2 \partial n_e / \partial \mu_e}$ is the screening parameter, μ_e is the electron chemical potential.

The Jancovici formalism for studying electrostatic energy was used only once in Ref.²⁶ where the bcc and fcc lattices were considered. Results for the hcp lattice are partly presented in Ref.²⁵ and will be published later. The electrostatic properties of binary and multicomponent lattices have never been studied.

The magnetic field does not effect directly to the electrostatic energy of Coulomb crystals but it changes the phonon spectrum and the screening parameter $\kappa\alpha$.³¹

4 | BINARY-COMPONENT LATTICES

Multicomponent lattices were investigated in a limited number of works. In Refs.^{32,33} electrostatic energies were computed using the Coldwell-Horsfall and Maradudin method.⁸ In Refs.^{34,35} binary-ionic mixtures were studied by Monte Carlo simulations. In Ref.¹² the Madelung constants of eight binary and one three-component lattices were obtained from limiting cases when a multicomponent lattice becomes a one-component one. Previously, Equation (2) was used in Refs.^{14,15} for binary body-centred and hcp lattices (with $h = h_0$). In the current paper, we use this equation for other lattices.

A binary body-centred lattice could be described as a sc lattice with two basis vectors. The basis vector $\chi_1 = 0$ corresponds to an ion with a charge number Z_1 , while the basis vector $\chi_2 = 0.5a_1(1, 1, 1)$ corresponds to an ion with a charge number Z_2 (the Cartesian coordinate system coincides with the lattice cube edges). We call this lattice an sc2 lattice, while in some papers^{11,34} it is marked as a CsCl lattice. The electrostatic energy of the sc2 lattice is

$$U_M = N \frac{Z_1^2 e^2}{a} \xi_{sc2} = N \frac{Z_1^2 e^2}{a} \left[\frac{1 + \alpha^2}{2^{4/3}} \xi_1 + \alpha \left(\xi_2 - \frac{\xi_1}{2^{1/3}} \right) \right], \quad (6)$$

where ξ_1 and ξ_2 are the Madelung constants of the sc and bcc lattices, respectively ($\xi_1 = \xi_{sc}$, $\xi_2 = \xi_{bcc}$), $\alpha \equiv Z_2/Z_1$. The number density of ions with Z_1 (n_1) is equal to the number density of ions with Z_2 (n_2), and the sc2 lattice stays the same under ion interchange ($Z_1 \leftrightarrow Z_2$ or $\alpha \leftrightarrow 1/\alpha$). Hence, we can numerate the ions such that $Z_2 \geq Z_1$ and consider $\alpha \geq 1$.

As it was done in Ref.¹² Equation (6) can be obtained from limiting cases when $Z_2 = Z_1$ and $Z_1 = 0$.¹⁵ The electrostatic energy of the sc2 lattice was also studied in Refs.^{32,33} analytically, and their results are consistent with our data. The results obtained in Refs.^{12,34,35} for the sc2 lattice are discussed later in the context of the linear mixing rule applicability in Section 8.

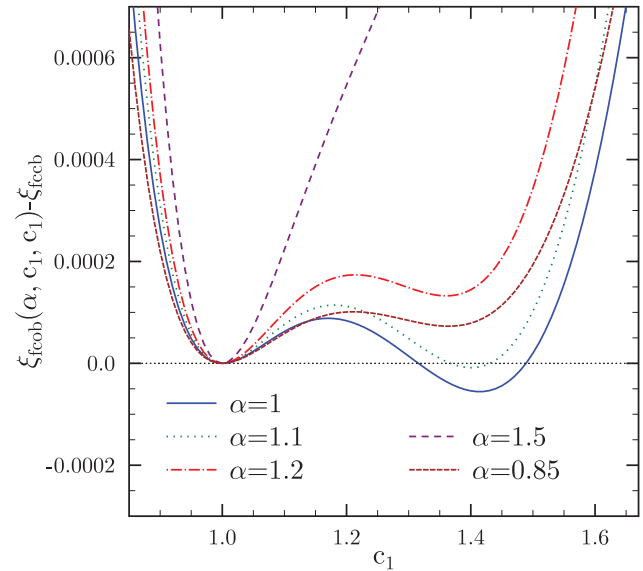
The binary face-centred cubic lattice (fccb) is an example of a lattice in which the number density of ions with Z_2 is three times larger than the number density of ions with Z_1 ($n_2 = 3n_1$). It is convenient to describe a fccb lattice as a simple lattice with the basis vectors $\chi_1 = 0$, $\chi_2 = 0.5a_1(1, 1, 0)$, $\chi_3 = 0.5a_1(0, 1, 1)$, and $\chi_4 = 0.5a_1(1, 0, 1)$. Thus, in this lattice, ions with a charge number Z_1 are located at the sites of the lattice cube and ions with a charge number Z_2 are in the centres of the faces. The electrostatic energy of a binary fcc lattice is

$$U_M = -N \frac{Z_1^2 e^2}{a} \xi_{fccb} = -N \frac{Z_1^2 e^2}{a} (0.138600677 + 0.1707354535\alpha + 0.5865374846\alpha^2). \quad (7)$$

For the first time it was calculated in Ref.³³ here it is presented with greater accuracy.

As it is known the bcc lattice is $\sqrt{2}$ times stretched along one of the elementary cell cube edges (for the chosen coordinate system in the current paper) and becomes the fcc lattice and vice versa. Hence, it is instructive to consider the electrostatic properties of a binary face-centred orthorhombic (fcob) lattice. The elementary cell of the fcob lattice is

FIGURE 1 Electrostatic energy of the face-centred orthorhombic lattice at $c_2 = c_1$



a rectangular prism with edges a_1 , b_1 , and c_1 , while its Madelung energy is

$$U_M = N \frac{Z_1^2 e^2}{a} \xi_{\text{fcob}}(\alpha, c_1, c_2), \quad (8)$$

where $c_1 \equiv b_1/a_1$ and $c_2 \equiv c_1/a_1$. For arbitrary c_1 and c_2 $\xi_{\text{fcob}}(\alpha, c_1, c_2)$ is not fitted, at small $|c_1-1|$ and $|c_2-1|$ it could be obtained from the elastic moduli.³⁶ For any fixed α in consideration the minimal value of $\xi_{\text{fcob}}(\alpha, c_1, c_2)$ always achieves at $c_2 = c_1$, but it is not necessary that this happens at $c_1 = 1$. For $c_2 = c_1$ and for some values of α $\xi_{\text{fcob}}(\alpha, c_1, c_2) - \xi_{\text{fccb}}$ is plotted in Figure 1, where $\xi_{\text{fccb}} = \xi_{\text{fcob}}(\alpha, 1, 1)$.

For any α and $c_1 = c_2 = 1$ the function $\xi_{\text{fcob}}(\alpha, c_1, c_2)$ has a local minimum; therefore, the binary fcc lattice is stable with respect to small stretches.¹ But only at $|\alpha - 1| \gtrsim 0.1$ the fccb lattice possesses the minimal energy among all binary face-centred orthorhombic lattices. The case $\alpha = 1$ was widely discussed in Ref.²⁴ $\xi_{\text{fcob}}(1, \sqrt{2}, \sqrt{2})$ corresponds to the Madelung constant of the bcc lattice and $\xi_{\text{bcc}} < \xi_{\text{fcc}}$. Figure 1 shows that for $|\alpha - 1| \lesssim 0.1$ minimum Madelung energy has a lattice with $c_1 \approx 1.4$. For example, at $\alpha = 1.1$ the minimum value is equal $\xi_{\text{fcob}}(\alpha, 1.40094, 1.40094) = -1.036128545$. The structure of this lattice is more similar to the bcc lattice if the difference in charges is neglected (the fccb and sc2 lattices cannot be compared directly). Therefore, it seems to us that any binary systems with small difference between Z_1 and Z_2 will form the bcc-like lattice.

The binary body-centred orthorhombic and other deformed sc2 lattices were studied in Ref.³⁶ Instead of the fccb lattice, the deformed sc2 lattice has the global minimum of energy at its cubic configuration at any fixed Z_1 and Z_2 .

One of the famous binary lattices which belongs to the cubic symmetry group is a NaCl lattice. In this lattice, some ions (charge number Z_1) form a fcc lattice, while others ions (charge number Z_2) form a similar fcc lattice, but shifted by the vector $0.5a_1(1, 1, 1)$ relatively to the first lattice (therefore, $n_1 = n_2$). At $Z_1 = Z_2$, the NaCl lattice becomes a sc lattice. For an arbitrary α , the electrostatic energy of the NaCl lattice is

$$U_M = -N \frac{Z_1^2 e^2}{a} (0.3555276798(1 + \alpha^2) + 0.1690040825\alpha), \quad (9)$$

which is consistent with results obtained in Refs.^{12,32} Only at $1/4.3 < \alpha < 4.3$, the Madelung energy of the sc2 lattice is less than the NaCl lattice energy.

One of the polymorphic modifications of silicon dioxide is called a β -cristobalite. Its lattice can be described as a sc lattice with 24 basis vectors. If we set $n_2 = 2n_1$ (in the elementary cell Si-like ions are marked as ions with the charge number Z_1), the Madelung energy of cristobalite could be written as

$$U_M = -N \frac{Z_1^2 e^2}{a} (0.1930839433 - 0.1014330353\alpha + 0.43098544745\alpha^2). \quad (10)$$

TABLE 1 Approximation parameters for the electrostatic energy of the h2 lattice

	m_0	m_1	m_2	m_3	m_4	m_5
$K_1(h)$	-0.16189364	-0.5579413	0.5939561	-0.3011056	0.08557277	-0.01011867
$K_2(h)$	-0.5115757	1.0714258	-1.1718758	0.56326835	-0.14312075	0.0150406

α	h_{h20}	ξ_{h20}
1.2	1.6	-1.0874421492
1.5	1.47435	-1.4230969646
2	1.2586	-2.1200861237

TABLE 2 h2 lattice: values of h_{h20} and $\xi_{h20}(\alpha)$ for several α

The cristobalite lattice labelled as θ -lattice was considered in Ref.¹¹ as one of the possible crystalline configurations of the neon-carbon mixture. However, in Ref.¹¹ the screened Coulomb potential was used to describe this and other lattices, which does not allow making an accurate comparison with our calculations. In addition, the electrostatic energy values are not specified in Ref.¹¹ At $Z_1 = Z_2$, the Madelung constant of cristobalite is equal -0.522636355 . For the one-component lattices, this value is the highest.

The sc2 lattice retains cubic symmetry at any α and this cubic configuration corresponds to the minimum energy (see Ref.²⁵ for details). For binary hexagonal lattices, the situation is more complicated. As in the one-component case, a binary hcp (h2) lattice could be described as a hexagonal lattice with two basis vectors. Vector $\chi_1 = 0$ corresponds to an ion with a charge number Z_1 , while the vector $\chi_2 = 0.5a_1(1, 1/\sqrt{3}, h)$ corresponds to an ion with charge number Z_2 . The number densities of ions of different types are equal ($n_1 = n_2$). The parameter h is not fixed and for $h \in (1.1; 1.8)$ the electrostatic energy of the h2 lattice could be fitted as

$$U_M = N \frac{Z_1^2 e^2}{a} \xi_{h2}(h) = N \frac{Z_1^2 e^2}{a} (K_1(h)(1 + \alpha^2) + K_2(h)\alpha), \quad (11)$$

$$K_{1,2}(h) = \sum_{i=0}^5 m_i h^i, \quad (12)$$

where the approximation parameters m_i are presented in Table 1.

For any fixed α , the electrostatic energy of the h2 lattice reaches its minimum at some $h = h_{h20}$ and h_{h20} decreases when the relative difference between the ion charges increases. This is illustrated in the Table 2, where the values of h_{h20} and $\xi_{h20} \equiv \xi_{h2}(h_{h20})$ for several α are shown. For any α in consideration, $\xi_{h20} > \xi_{sc2}$.

For the h2 lattice with fixed $h = \sqrt{8/3}$ the electrostatic energy could be written by Equation (6), where ξ_1 and ξ_2 are Madelung constants of the hex and hcp lattices, respectively ($\xi_1 = \xi_{hex}$, $\xi_2 = \xi_{hcp}$). This equation was previously obtained in Refs.^{12,33}

A more complex structure has a magnesium diboride (MgB_2) lattice. Previously, this lattice was considered in Ref.¹¹ where it was called a γ -lattice. The MgB_2 lattice can be described as a hexagonal lattice with the main translation vectors: $\mathbf{a}_1 = a_1(1, 0, 0)$, $\mathbf{a}_2 = 0.5a_1(1, \sqrt{3}, 0)$, $\mathbf{a}_3 = a_1(0, 0, \tilde{h})$ and with three basis vectors: $\chi_1 = 0$, $\chi_2 = 0.5a_1(1, 1/\sqrt{3}, \tilde{h})$ and $\chi_3 = a_1(1, 1/\sqrt{3}, 0.5\tilde{h})$. The vector χ_1 corresponds to an ion with a charge number Z_1 . The number density of such ions n_1 is two times lower than the number density of ions with a charge number Z_2 (n_2 , vectors χ_2 and χ_3). The distance between the layers of ions with the same charge number in units of a_1 is denoted as \tilde{h} . It is not fixed (for a crystal in terrestrial conditions $\tilde{h} \approx 1.142$). Therefore, the electrostatic energy of a binary MgB_2 crystal for $0.5 \leq \tilde{h} \leq 1.85$ could be approximated as:

$$U_M = N \frac{Z_1^2 e^2}{a} \xi_{MgB_2}(\tilde{h}) = N \frac{Z_1^2 e^2}{a} (K_1(\tilde{h}) + K_2(\tilde{h})\alpha + K_3(\tilde{h})\alpha^2), \quad (13)$$

$$K_{1,2,3}(\tilde{h}) = \sum_{i=0}^7 m_i \tilde{h}^i, \quad (14)$$

where parameters $K_1(\tilde{h})$, $K_2(\tilde{h})$, and $K_3(\tilde{h})$ are presented in Table 3.

TABLE 3 Approximation parameters for the electrostatic energy of the MgB₂ lattice

	m_0	m_1	m_2	m_3	m_4	m_5	m_6	m_7
$K_1(\tilde{h})$	0.383321	3.09006	7.21763	-9.63175	7.80169	-3.7803	1.00879	-0.114044
$K_2(\tilde{h})$	-0.677904	1.87234	-3.26584	3.70539	-2.97767	1.51651	-0.430256	0.0514738
$K_3(\tilde{h})$	0.381939	-4.85327	11.5234	-15.4381	12.646	-6.19333	1.66776	-0.189958

TABLE 4 MgB₂ lattice: values of $\tilde{h}_{\text{MgB}_2,0}$ and $\xi_{\text{MgB}_2,0}$ for several α

α	$\tilde{h}_{\text{MgB}_2,0}$	$\xi_{\text{MgB}_2,0}$
0.2	1.028	-0.2641376075
0.4	0.914	-0.3600172447
0.5	0.729	-0.42325073365
0.75	0.619	-0.62771700828
1	0.593936	-0.89450562823
1.25	0.591	-1.22218432727
1.5	0.595	-1.61057883013
1.75	0.601	-2.0597607806
2	0.607	-2.56981540483

We denote the height of the MgB₂ lattice, at which the minimum value of $\xi_{\text{MgB}_2}(\tilde{h})$ reaches, as $\tilde{h}_{\text{MgB}_2,0}$ and mark $\xi_{\text{MgB}_2,0} \equiv \xi_{\text{MgB}_2}(\tilde{h}_{\text{MgB}_2,0})$. From Table 4, it can be seen that the dependence $\tilde{h}_{\text{MgB}_2,0}$ does not change monotonically with α (see Figure 7). At $Z_1 = Z_2$, the Madelung constant of magnesium diboride is equal to -0.89450562823 . This is more than the Madelung constant of bcc, fcc, and hcp lattices, but less than others.

5 | MULTICOMPONENT LATTICES

Madelung energies of several lattices, which consist of three or four types of ions, are also studied. All of these lattices were investigated earlier^{11,12} or are natural generalizations of more special cases.

Electrostatic energy of a three-component perovskite lattice is

$$U_M = -N \frac{Z_1^2 e^2}{a} (0.102932376777(Z_1^2 + Z_2^2) + 0.058185774325Z_1Z_2 + 0.020881575292Z_1Z_5 + 0.126797403936Z_2Z_5 + 0.435594534266Z_5^2). \quad (15)$$

For the chosen configuration, the basis vector χ_1 corresponds to an ion with a charge number Z_1 , for $p = 2, 3, 4$ $Z_p = Z_2$ and the basis vector χ_5 corresponds to an ion with a charge number Z_5 (see paragraph 3). Hence $n_2 = 3n_1 = 3n_5$, where n_5 is the number density of ions with Z_5 . Equation (15) correctly reproduces limiting cases and is consistent with the results obtained in Ref.¹²

In the general case, if all symmetries are taken into account, the fluorite lattice can be developed up to a three-component lattice of some hypothetical compound AB₃C₈. We use the same basis vectors as for the one-component case. In the three-component fluorite vector, χ_1 corresponds to an ion with a charge number Z_1 , for $p = 2, 3, 4$ $-Z_p = Z_2$, and $Z_p = Z_5$ at $p = 5, \dots, 12$. The Madelung energy of the three-component fluorite is

$$U_M = -N \frac{e^2}{a} (0.03203344735Z_1^2 + 0.1355607926Z_2^2 + 0.51253515762Z_5^2 + 0.03946045054Z_1Z_2 + 0.03621583406Z_1Z_5 + 0.10864750219Z_2Z_5). \quad (16)$$

Equation (16) correctly reproduces all limiting cases. For instance, at $Z_5 = 0$ this lattice becomes an fccb lattice. The case of two-component fluorite at $Z_1 = Z_2$ is more important because CaF₂ form this lattice (it was considered in Ref.¹²).

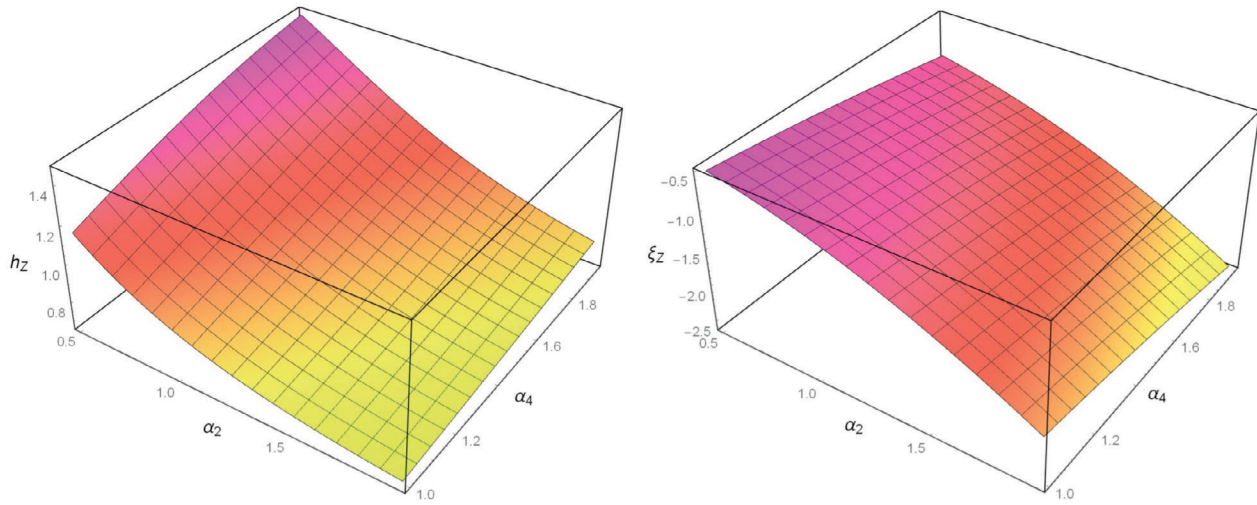


FIGURE 2 ζ -lattice: dependence h_Z and ξ_Z from α_2 and α_4

In a three-component diamond lattice, an ion with a charge number Z_1 is located at a lattice site with χ_1 , ions with a charge number Z_2 are located at lattice sites with χ_{2-4} , and ions with a charge number Z_5 are in the rest of the lattice sites (see paragraph 3), $n_5 = 4n_1$ and $n_2 = 3n_1$. The electrostatic energy of this lattice is

$$U_M = -N \frac{e^2}{a} (0.05500371513Z_1^2 + 0.23276755503Z_2^2 + 0.3555276798Z_5^2 + 0.06775640963Z_1Z_2 + 0.09327775738Z_1Z_5 + 0.03109258579Z_2Z_5). \quad (17)$$

At $Z_2 = Z_1$, the number density of ions with a charge number Z_5 is equal to the number density of the rest of the ions. The Madelung energy of such binary diamond at any α is greater than U_M of the sc2 lattice.

Among all hexagonal lattices, we consider the Madelung energies of two crystals mentioned in Ref.¹¹: the ζ -lattice (FeOC_2) and the η -lattice (FeO_3C_2).

The ζ -lattice can be described as a hexagonal lattice (the main translation vectors are the same as for the hcp lattice) with four basis vectors: the vector $\chi_1 = 0$ corresponds to an ion with a charge number Z_1 ; vectors $\chi_2 = 0.5a_1(1, 1/\sqrt{3}, 0)$ and $\chi_3 = a_1(1, 1/\sqrt{3}, 0)$ correspond to ions with a charge number Z_2 , while $\chi_4 = 0.5a_1(0, 0, h)$ corresponds to an ion with a charge number Z_4 . The lattice does not change under replacement $Z_4 \leftrightarrow Z_1$ so ions are numbered such that $Z_4 \geq Z_1$. For fixed $\alpha_2 \equiv Z_2/Z_1$ and $\alpha_4 \equiv Z_4/Z_1$, we choose the elementary cell height $h = h_Z$ such that U_M is minimal. The Madelung energy of a ζ -lattice can be presented as

$$U_M = N \frac{Z_1^2 e^2}{a} \xi_Z. \quad (18)$$

The dependence of h_Z and ξ_Z on α_2 and α_4 are shown in Figure 2. For $Z_4 = Z_2 = Z_1$ the Madelung constant is equal -0.8242044637442 and $h_Z \approx 0.867108$.

Similarly the η -lattice can be described as a hexagonal lattice with six basis vectors: $\chi_1 = 0$, $\chi_2 = a_1(1, 1/\sqrt{3}, 0)$, $\chi_3 = 0.5a_1(1, 1/\sqrt{3}, 0)$, $\chi_4 = 0.5a_1(1, 0, h)$, $\chi_5 = 0.5a_1(3/2, \sqrt{3}/2, h)$, and $\chi_6 = 0.5a_1(5/2, \sqrt{3}/2, h)$. They correspond to ions with charge numbers: Z_1, Z_2, Z_2, Z_4, Z_4 , and Z_4 , respectively. In this lattice, the nonfixed h is chosen from the condition of electrostatic energy minimum: $h = h_{\text{ET}}$. h_{ET} is plotted in left part of Figure 3. The Madelung energy of a η -lattice can be written as

$$U_M = N \frac{Z_1^2 e^2}{a} \xi_{\text{ET}}. \quad (19)$$

The dependence of ξ_{ET} at $h = h_{\text{ET}}$ on α_2 and α_4 is shown in right part of Figure 3. For $Z_4 = Z_2 = Z_1$, the Madelung constant is $\xi_{\text{ET}} = -0.8721352931537$ and $h_{\text{ET}} = 0.95162$.

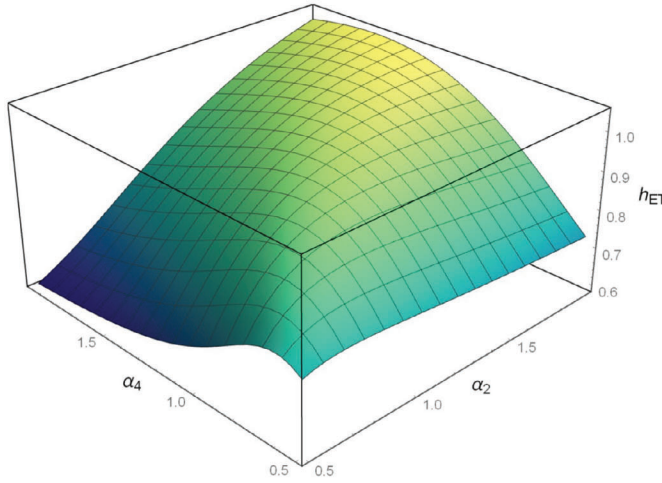


FIGURE 3 η -lattice: dependence h_{ET} and ξ_{ET} from α_2 and α_4

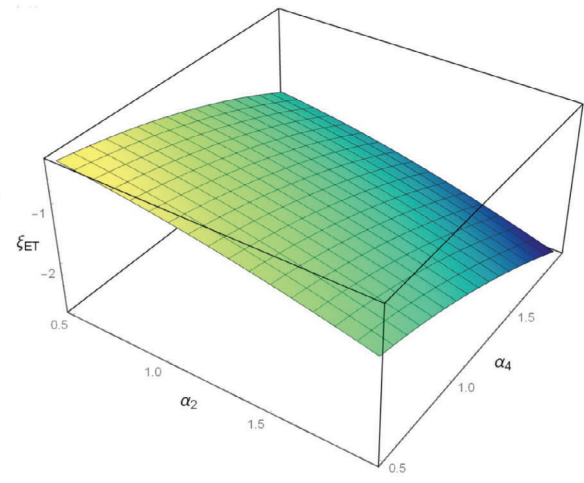
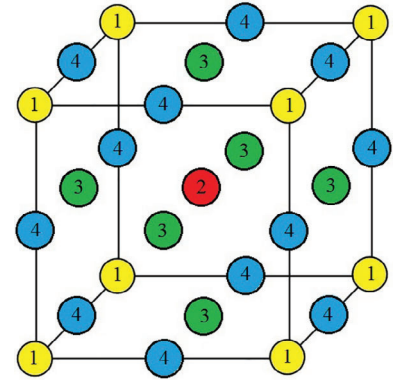


FIGURE 4 A forth-component Dyson lattice



Totally eight lattices were considered in Ref.¹¹: four were mentioned above (θ -, γ -, ζ -, and η -lattices); one-component bcc (α -lattice) and sc2 (β -lattice) lattices have already been discussed; the orthorhombic δ -lattice and the tetragonal ϵ -lattice are not studied in our paper. The investigation of the last two lattices requires consideration of a large number of unfixed lattice parameters. For instance, the δ lattice could be presented as a deformed NaCl lattice.

Most cubic lattices can be summarized in a forth-component Dyson lattice.^{12,32} This lattice is shown in Figure 4: different numbers and colours indicate different types of ions. Thus, yellow ions have a charge number Z_1 , red— Z_2 , green— Z_3 , and blue— Z_4 , while a_1 is the distance between two nearest Z_1 ions. The electrostatic energy of the fourth-component Dyson lattice calculated using Equation (2) is

$$U_M = -N \frac{e^2}{a} (0.0550037151(Z_1^2 + Z_2^2) + 0.232767555(Z_3^2 + Z_4^2) + 0.0310925858Z_1Z_2 + 0.0677564096(Z_1Z_3 + Z_2Z_4) + 0.0111584348(Z_2Z_3 + Z_1Z_4) + 0.115594627Z_3Z_4). \quad (20)$$

This equation reproduces the energies of many lattice with an accuracy of 9 significant digits (if the number density changes are taken into account). For instance, at $Z_3 = Z_4 = 0$ this is the energy of the sc2 lattice, while at $Z_1 = Z_3$ and $Z_2 = Z_4$ —of the NaCl lattice. At $Z_1 = Z_2$ and $Z_3 = Z_4$ Equation (20) is consistent with the results obtained in Refs.^{12,32}

6 | ENERGY OF ZERO-POINT VIBRATIONS

The energy of zero-point vibrations (U_0) is not considered in this paper in detail. For the one-component lattice

$$U_0 = 1.5N\hbar\langle\omega\rangle = 1.5N\hbar\omega_p u_1, \quad (21)$$

where $\langle \omega \rangle$ is the phonon frequency averaged over the first Brillouin zone, $\omega_p = \sqrt{4\pi n Z^2 e^2 / M}$ is the ion plasma frequency, M is the ion mass, u_1 is called a first phonon-spectrum moment. For the bcc lattice $u_1^{\text{bcc}} = 0.5113877$, and for the hcp lattice $u_1^{\text{hcp}} = 0.513194$. For the one-component crystal, the sum of the electrostatic and zero-point energies is

$$E_0 = N \frac{Z^2 e^2}{a} \xi + 1.5 N \hbar \frac{\sqrt{3} Z e}{a^{1.5}} u_1, \quad (22)$$

$$\frac{E_0}{N T_p} = \Gamma_p \xi + 1.5 u_1, \quad (23)$$

where $T_p = \hbar \omega_p$ is the ion plasma temperature and $\Gamma_p \equiv Z^2 e^2 / (a \hbar \omega_p) = Z e \sqrt{M} (36 \pi n)^{-1/6} / \hbar$. For typical densities in the envelopes of neutron stars and white dwarfs, $\Gamma_p > 10$ for the carbon plasma and $\Gamma_p > 100$ for iron. Hence, $|\xi \Gamma_p| \gg 1.5 u_1$. However, for bcc, fcc, and hcp lattices, the difference between the Madelung constants is much smaller than the difference between the first moments. For example, for bcc and fcc lattices $|\Delta \xi| \approx 0.00005564$, while $|\Delta u_1| \approx 0.00181$ and $|\Delta \xi \Gamma_p| \approx |1.5 \Delta u_1|$. Therefore, in some cases the zero-point energy can play an important role.

Among all one-component lattices with isotropic pressure, the lowest zero-point energy has the bcc lattice and this lattice has the lowest total sum of energies. As it was shown in Ref.²⁵ in some cases, U_0 of the deformed bcc lattice is less than U_0 of the bcc lattice, which, in turn, leads to the fact that at some densities the sum of the electrostatic and zero-point energies of this deformed bcc lattice becomes smaller than that of the undeformed bcc lattice. On the other hand, the electrostatic pressure in deformed lattices is not isotropic in the general case, and it is incorrect to compare them with lattices with isotropic pressure.

The sc2 and h2 (with $h = h_{h20}$) lattices are best suited to study the influence of the energy of zero-point vibrations on the total crystal energy of binary crystals. Comparison of such lattices is possible only when their ionic composition is the same and the hcp lattice has the third lowest electrostatic energy among all one-component lattices. The first moment of binary lattices depends on two parameters α and the ratio between masses of ions in the elementary cell $\beta \equiv M_2 / M_1$. For the sc2 and h2 lattices, $u_1(\alpha, \beta)$ was plotted in Refs.^{15,25} and fitted for sc2 lattice in Ref.²⁵ The difference between sums of electrostatic and zero-point energies of the sc2 and h2 lattices is

$$\Delta E_0 = N \frac{Z_1^2 e^2}{a} \Delta \xi(\alpha) + 1.5 N \hbar \omega_s \Delta u_1(\alpha, \beta), \quad (24)$$

where $\Delta \xi(\alpha) \equiv \xi_{\text{sc2}} - \xi_{\text{h20}}$, $\Delta u_1(\alpha, \beta)$ is the difference between the first moments of these lattices, $u_1(\alpha, \beta) \equiv \langle \omega / \omega_s \rangle$, $\omega_s \equiv \sqrt{\pi n_1 Z_1^2 e^2 (1 + \alpha)(1 + \alpha / \beta) / M_1}$.

For binary crystals, ΔE_0 could be considered as a function of Γ_{p1} , α and β , where $\Gamma_{p1} \equiv Z_1^2 e^2 / (a_1 \hbar \omega_{p1})$, $\omega_{p1} \equiv \sqrt{4\pi n_1 Z_1^2 e^2 / M_1}$ is the plasma frequency of ions with the charge number Z_1 and mass M_1 , $a_1 \equiv (4\pi n_1 / 3)^{-1/3}$. Note that the parameter Γ_{p1} is determined by the first type ions and their number density n_1 , while the density of the crystal depends on M_1 and β .

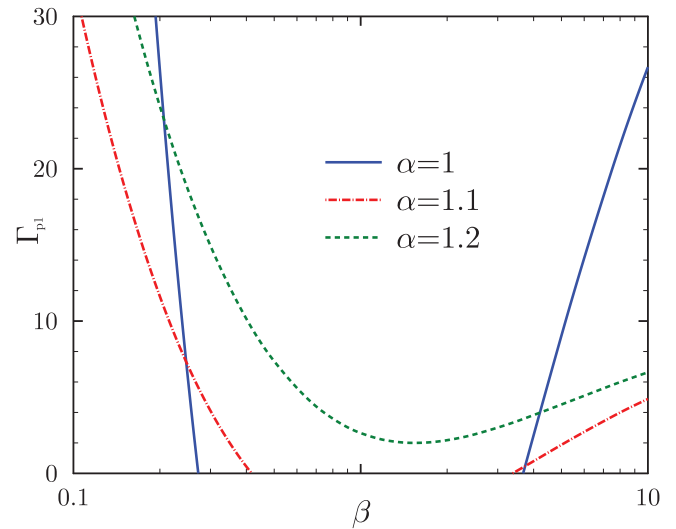
In Figure 5, we show the dependencies of Γ_{p1} corresponding to $\Delta E_0 = 0$ on β for a fixed α . For Γ_{p1} lying above these curves an sc2 lattice ($\Delta E_0 < 0$) is more energetically favourable, below—the h2 lattice ($\Delta E_0 > 0$). As $\Gamma_{p1} \gtrsim 10$ in the degenerate stars, the h2 lattice corresponds to exotic compounds and their formation there is unlikely.

In the current paper, we are not going to discuss the phonon thermal properties of Coulomb crystals. For the sc2 lattice, they were widely studied in Ref.¹⁵ while the properties of the h2 lattice with $h = h_{h20}$ are slightly differ from the properties of the h2 lattice with fixed $h = \sqrt{8/3}$, which were studied in Ref.¹⁵

It seems that in the envelopes of hot degenerate stars, formation of the sc2 lattice is more likely, and the transition to the h2 lattice during the cooling of the star is possible only for a small number of ionic mixtures.²⁵

7 | PHONON STABILITY

All lattices under consideration must be stable against small ion oscillations around equilibrium positions. The phonon spectrum of a Coulomb crystal should not possess modes with $\omega^2 < 0$ at any wavevector \mathbf{k} . The phonon spectrum could be obtained from the dispersion equation $\det\{D_{pp'}^{\mu\lambda}(\mathbf{k}) - \omega^2 \delta^{\mu\lambda} \delta_{pp'}\} = 0$, where $D_{pp'}^{\mu\lambda}(\mathbf{k})$ is the dynamic

FIGURE 5 Dependence Γ_{pl} from α and β 

matrix. In a convenient form, the dynamic matrix of any strongly ordered multicomponent lattice can be found in Ref.¹⁵

The stability of one-component Coulomb lattices was discussed earlier. The bcc and fcc lattices are stable, while the sc lattice are not. A sc lattice is known to be unstable for a long time. Notice that no direct proof of this statement has been found in the literature. In a series of Born papers, which is usually referred in this context³⁷ among all considered potentials was not purely Coulomb. Therefore, for the first time the phonon spectrum of the sc Coulomb lattice was presented in Ref.²⁵ The hex lattice is unstable too, while the hp lattice is stable at $1.48 < h < 1.82$.

The stability of deformed bcc and fcc lattices was widely studied in Refs.^{24,25} where it was shown that the bcc lattice stretched 1.49 times along one of the elementary cell cube edges (towards the second nearest neighbour), remains stable. Hence, it is possible to translate the bcc lattice into the fcc lattice by continuous deformation. On the other hand, compression in the same direction is possible only by 6.5%. The bcc lattice which stretched along its main diagonal (in the direction of the nearest neighbour) is stable when $0.92 < c_{d1} < 1.13$, where c_{d1} is the ratio of the length of the diagonal along the deformation to the length of the undeformed diagonal.²⁴ Stretched along the diagonal of the base of the elementary cell cube (towards the third nearest neighbour), the bcc lattice is stable when c_{d3} lies between 0.9 and 1.06, where c_{d3} is the similar ratio as in the previous case but for the base diagonal.

In the bcc lattice with a shift, vector $a_1(0, 0, 1)$ turns to the vector $a_1(c_x, c_y, 1)$. The volume of the elementary cell does not change with this deformation. Instead of electrostatic energy, the stability of a bcc lattice with a shift cannot be considered as a function of $\sqrt{c_x^2 + c_y^2}$. Noticeable anisotropy is present. At $c_y = c_x$ lattice loses stability at $c_x = 0.09$, while at $c_y = 0$ this happens at $c_x = 0.14$ and $\sqrt{c_x^2 + c_y^2}$ changes from 0.127 to 0.14.

Thus, the stability of the bcc lattice substantially depends on the direction of deformation. In all cases under consideration, instabilities appear in the centre of the first Brillouin zone in certain wave vector directions. The region of wave vectors with $\omega^2 < 0$ increases with increasing the value of the crystal deformation. The evolution of these regions was considered in Refs.²⁴

The stability of other one-component Coulomb lattices was not studied in detail. We find that in addition to sc and hex lattices, simple rhombic and tetragonal, as well as base-centred rhombic and monoclinic lattices are unstable. A shallow analysis shows that the remaining Bravais lattices (simple monoclinic, triclinic, and rhombohedral) are also unstable in a wide range of parameters.

The stability of undeformed multicomponent lattices depends on the charge ratio between ions in the elementary cell and does not depend on their masses. The phonon spectrum of the simplest binary Coulomb lattices was studied in Refs.^{14,15} The phonon spectrum analysis implies that the sc2 lattice is unstable at $\alpha < 3.6$ ($\alpha \geq 1$ by definition). Similar limits $1/3.596 < \alpha < 3.596$ were recently found (but later than paper¹⁴ was published) from molecular dynamics simulations in Ref.³⁸

The stability of the deformed sc2 lattice can be studied as a function of the direction and magnitude of the deformation, as well as parameter α . Among all deformed sc2 lattices, we consider only a binary sc2 lattice stretched along one of the edges of its elementary cell, \tilde{c}_1 is the relative stretch in units of a_1 (similarly to the fcob lattice from paragraph 4). The

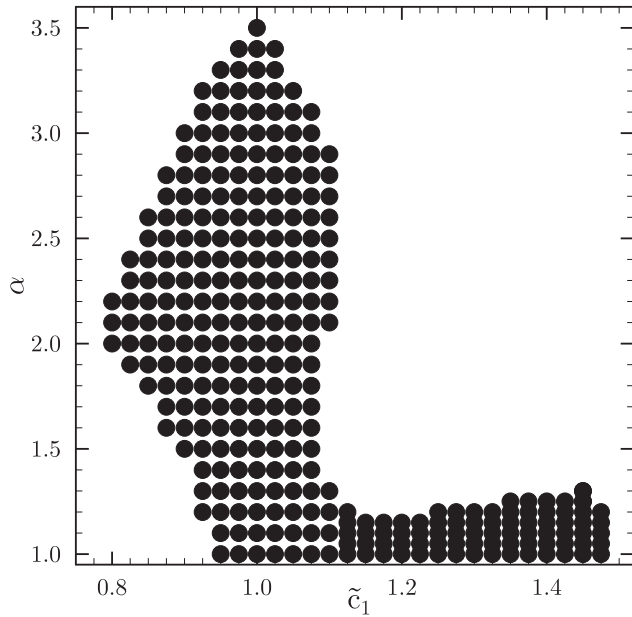


FIGURE 6 The range of values α and \tilde{c}_1 for which the deformed sc2 lattice is stable

phonon spectrum of this lattice consists of six modes and has the same features as the spectrum of the sc2 lattice. The range of parameters α and \tilde{c}_1 , at which the deformed sc2 lattice is stable, is shown in Figure 6. Each point shows a set of parameters at which investigations were carried out. When \tilde{c}_1 changes, the range of α changes but it always remains between 1 and 3.6.

The properties of the h2 lattice with fixed $h = \sqrt{8/3}$ were studied in Refs.^{14,15} This lattice is stable at $\alpha \leq 1.25$. If we use $h = h_{h20}$ instead of $\sqrt{8/3}$, this limit will not noticeably change and the lattice will become unstable at $\alpha = 1.26$.

The phonon spectrum of the fcb lattice, described as a simple lattice with four basis vectors, consists of 12 modes. It is stable at $0.66 \leq \alpha \leq 1.38$ (the step over α is 0.02). This result is consistent with the restrictions given in Ref.³⁸: $0.661 \leq \alpha \leq 1.368$.

The phonon spectrum of the MgB_2 lattice consists of nine modes (\tilde{h} is not fixed). The one-component MgB_2 lattice is unstable. This lattice becomes stable when the charge of ions with a higher number density is considerably less than the charge of other ions. The range of α and \tilde{h} for the stable MgB_2 lattice is shown in Figure 7. It can be seen that α does not exceed 0.375 (the step over α is 0.025), and \tilde{h} varies from 0.85 to 1.35 (the step over \tilde{h} is 0.025). Note that for all considered α , except $\alpha = 0.375$, the dependence $\tilde{h}_{\text{MgB}_2,0}$ (see Section 4) lies in the region of lattice stability. In Figure 7, the dependence $\tilde{h}_{\text{MgB}_2,0}$ on α is shown by a solid blue line.

The phonon spectrum of a binary NaCl lattice consists of six modes. It is stable at $\alpha \geq 3.9$. For $\alpha = 1$, this lattice becomes an unstable sc lattice, and for $\alpha = \infty$ it is a stable fcc lattice.

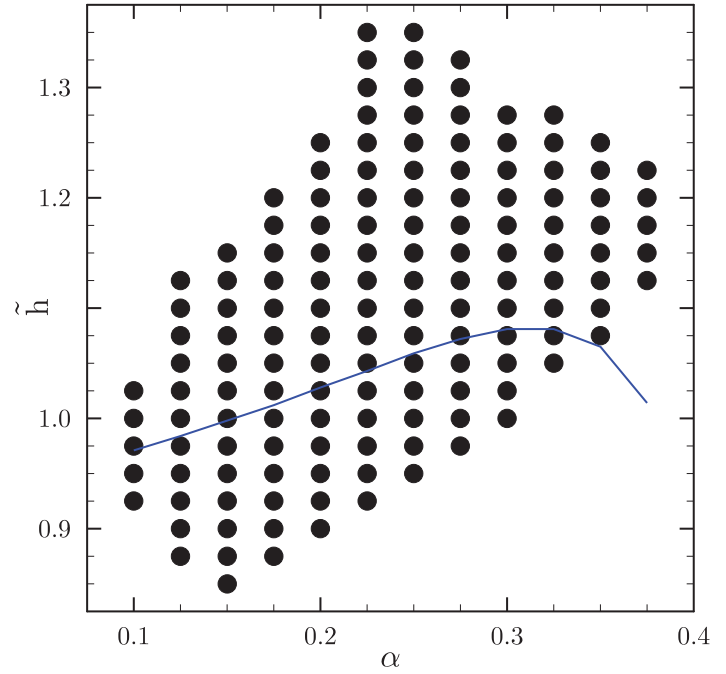
The Dyson binary lattice with $Z_1 = Z_2$ and $Z_3 = Z_4$ is not stable at $\alpha \sim 1$. The stability of the four component Dyson lattices was not studied in detail. It is known that it is stable in limiting cases, for example, at $Z_3 = Z_4 = 0$ as a sc2 lattice, but for $Z_3 \neq 0$ and/or $Z_4 \neq 0$ it quickly loses stability. Thus, already at $Z_2 = Z_1, Z_3 = 0.025Z_1, Z_4 = 0.025Z_1$ complex-valued frequencies appear. Similarly, at $Z_2 = Z_4 = 0$ the Dyson lattice is stable because the binary fcc lattice is stable, but even at $Z_2 = 0, Z_3 = Z_1, Z_4 > 0.1Z_1$ it loses stability.

8 | LINEAR MIXING RULE

The second condition for the formation of a stable multicomponent crystal is a resistance to separation into one-component crystals. The electrostatic energy of a multicomponent crystal should be less than the energy of a set of one-component bcc lattices calculated via so-called “linear mixture rule”. According to the “linear mixing rule” (lm), the electrostatic energy of a binary crystal mixture is

$$U_M^{\text{lm}} = N_1 \frac{Z_1^2 e^2}{a_1} \xi_{\text{bcc}} + N_2 \frac{Z_2^2 e^2}{a_2} \xi_{\text{bcc}}, \quad (25)$$

FIGURE 7 The range of α and \tilde{h} for which the MgB₂ lattice is stable. The curve is the dependence of $\tilde{h}_{\text{MgB}_2,0}$ on α



where N_i and n_i are the number and number density of ions with charge number Z_i . The effective ion sphere radius a_j is chosen such that the electron number density in each component of the mixture is equal to the total electron number density in the entire mixture $a_j = (4\pi n_j/3)^{-1/3} = a(Z_j/\bar{Z})^{-1/3}$, $\bar{Z} \equiv (n_1 Z_1 + n_2 Z_2)/n$ is the averaged charge number. We can use any Madelung constant instead of ξ_{bcc} (as it was done in Refs.^{15,25} where the type of the lattice was the same for binary and one-component lattices). Here, we choose the bcc lattice because this lattice possesses the lowest electrostatic energy among all one-component lattices.

Equation (25) could be rewritten as

$$U_{\text{M}}^{\text{lm}} = N \frac{Z_1^2 e^2}{a} \frac{(n_1 + n_2 \alpha)^{1/3}}{n^{4/3}} (n_1 + n_2 \alpha^{5/3}) \xi_{\text{bcc}}. \quad (26)$$

In this form, it could be used for any binary lattice. The ratio between the energy of the sc2 lattice and the energy of two one-component bcc lattices according to lm is

$$\frac{U_{\text{M}}^{\text{lm}}}{U_{\text{M}}} = \frac{(1 + \alpha)^{1/3} (1 + \alpha^{5/3}) \xi_{\text{bcc}}}{(1 - \alpha)^2 \xi_{\text{sc}} + 2^{4/3} \alpha \xi_{\text{bcc}}}. \quad (27)$$

The dependence of $10(U_{\text{M}}^{\text{lm}} - U_{\text{M}})/U_{\text{M}}$ on α for the sc2 lattice is shown in Figure 8. Multiplier 10 is used to show that the ratio $(U_{\text{M}}^{\text{lm}} - U_{\text{M}})/U_{\text{M}}$ is an order of magnitude smaller than the relative difference between the energies of the sc2 and h2 (with $h = h_{\text{h}20}$) lattices, which is shown in Figure 8. For the $^{16}\text{O} + ^{12}\text{C}$ mixture, the relative difference is $U_{\text{M}}^{\text{lm}}/U_{\text{M}} - 1 \approx -6.7 \times 10^{-5}$, and in the maximum permissible $\alpha = 3.6$ the maximum value reaches: $U_{\text{M}}^{\text{lm}}/U_{\text{M}} \approx 1.00094$. Thus, lm allows one to calculate the electrostatic energy of the sc2 lattice with an accuracy of 3–4 significant digits (depending on α).

Previously, lm for Madelung energy was investigated in Ref.³⁴ where the relative difference between U_{M}^{lm} and the electrostatic energy of a fully ordered sc2 crystal obtained from numerical simulations of a system of 432 ions (Δu) was calculated.

$$\Delta u \equiv \frac{U_{\text{M}}^{\text{lm}} - U_{\text{M}}}{NZ_1^2 e^2 / a_1} = \frac{0.5(1 + \alpha^2) \xi_{\text{sc}} + \alpha(2^{1/3} \xi_{\text{bcc}} - \xi_{\text{sc}})}{(1 + \alpha)^{1/3}} - 0.5 \xi_{\text{bcc}} (1 + \alpha^{5/3}). \quad (28)$$

As it could be seen from Table 5 these numerical results are in a good agreement with our analytical results obtained from Equation (27).

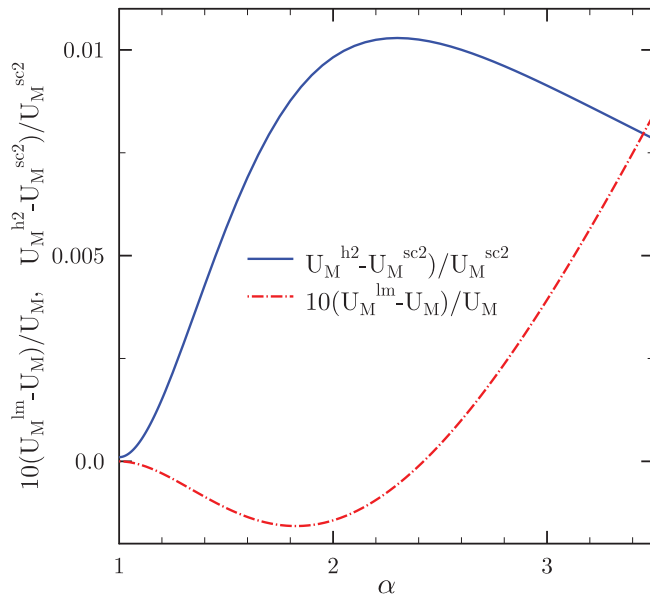


FIGURE 8 The relative difference between the precise result and the result obtained via lm for the sc2 lattice

α	Δu obtained from Equation (27)	Δu from Ref. ³⁴
4/3	-0.0000781	-0.00006
5/3	-0.000219	-0.00019
2	-0.000268	-0.00024
3	0.00127	0.00134
4	0.00668	0.00678

TABLE 5 Values of Δu for the sc2 lattice and several α

Note that in Ref.³⁴ it was shown that the difference between the electrostatic energy of the binary bcc lattice, in which (unlike in the sc2 lattice) for fixed α and n_1 the type of the ion in the lattice site was chosen randomly, and the energy obtained from the “linear mixing rule” is an order of magnitude greater than in the case under our consideration (strongly ordered sc2 lattice). Moreover, $\Delta u > 0$ for any α and n_1 , which looks strange enough.

$U_M^{lm} \leq U_M$ at $1/2.4229 < \alpha < 2.4229$ for the sc2 lattice. The energy of the sc2 crystal is less than the sum of the energies of two one-component lattices; therefore, the formation of a binary crystal at such α and $T = 0$ is energetically more favourable. Accordingly, at $\alpha > 2.4229$ and $\alpha < 1/2.4229$ for the sc2 lattice it is more advantageous to decompose it into two one-component bcc lattices. This range of values was obtained in Ref.³² for the first time.

In Ref.³² in addition to the sc2 lattice stability of the NaCl and two-component Dyson ($Z_1 = Z_2$ and $Z_3 = Z_4$) lattices were considered. However, as it was mentioned in the previous paragraph the two-component Dyson lattice is not stable to phonon oscillations at $\alpha \sim 1$, while the NaCl crystal lattice will meet both stability criteria at $\alpha > 5.197$.

The approach from Ref.³² was developed in Ref.^{35,39} for disordered two-component crystals and for AB_3 type crystals (two-component Dyson, fccb, and one more lattice, which is not studied here). For the fccb lattice, the relation U_M^{lm}/U_M is always greater than 1 so it is not stable as well as the h2 lattice with $h = h_{h20}$, which has never been studied before. Rough analysis of the MgB_2 lattice stability shows that at $\tilde{h}_{MgB_2,0}$ it is stable at $0.1 < \alpha < 0.32$.

9 | CONCLUSIONS

We summarized all information about the electrostatic energies of different Coulomb crystals both one-component and multicomponent. If earlier these energies were obtained by various disparate methods, in this work the one universal equation (Equation 2) was used. Among all one-component crystals, the bcc lattice possesses the lowest energy. Its Madelung constant is -0.895929255682 .

The electrostatic properties of multi-component Coulomb crystals depend not only on the charge numbers and number densities of the ions from which they are formed but also more important, on the geometry of its crystal lattice. For

instance, in the h2 lattice the distance between the hexagonal layers, at which the minimum of electrostatic energies reaches, decreases when the relative difference between the ion charges increases. While at $|\alpha - 1| \lesssim 0.1$ ($\alpha = Z_2/Z_1$), the minimum energy of the fcob lattice does not correspond to a crystal with a cubic symmetry (the fcob lattice).

For the sc2 and h2 lattice, we calculated the first moment of the phonon spectrum and obtained that for some number densities and composition of ions the sum of the electrostatic energy and the energy of the zero-point vibrations of the h2 lattice is less than the same sum for the sc2 lattice. Consequently, the formation of the h2 lattice at such parameters is more energetically preferable. Unfortunately, these parameters are not typical for the envelopes of degenerate stars.

All lattices must be stable against small oscillations of the ions around their equilibrium positions. We studied stability of different Coulomb lattices with isotropic electrostatic pressure. It was found that the sc2 lattice is stable at $\alpha < 3.6$, while the binary NaCl lattice is stable at $\alpha \geq 3.9$. In addition, for some deformed lattices limits of deformation were obtained. All previous results were successfully reproduced.

Multicomponent crystals must also be stable against separation into set of one-component lattices. Their energy should be less than the energy of set of one-component lattices calculated according to the linear mixing rule. It turned out that the h2 lattice does not satisfy this condition at any α . For the sc2 lattice α must be less than 2.4229.

If we complete all results we can conclude that for binary systems with $n_1 = n_2$ for $1/2.4229 < \alpha < 2.4229$, ions can form a sc2 lattice, and for $\alpha > 5.197$ and $\alpha < 0.192$ they can form a binary NaCl lattice; no stable lattices were found in the rest of the ranges. However, for $0.1 < \alpha < 0.32$, the MgB₂ lattice is stable (it has $n_2 = 2n_1$).

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REFERENCES

- [1] C. Kittel, Introduction to Solid State Physics, Wiley, Hoboken **2004**.
- [2] V. Fortov, A. Ivlev, S. Khrapak, A. Khrapak, G. Morfill, *Phys. Rep.* **2005**, 421(1–2), 1.
- [3] V. Fortov, G. Morfill, Complex and Dusty Plasmas: From Laboratory to Space, CRC, Portland **2009**.
- [4] S. Shapiro, S. Teukolsky, Black Holes, White Dwarfs, and Neutron Stars, Wiley-Interscience, New York, NY **1983**.
- [5] P. Haensel, A. Potekhin, D. Yakovlev, Neutron Stars 1: Equation of State and Structure, Springer, New York, NY **2007**.
- [6] K. Fuchs, *Math. Phys. Sci.* **1935**, 151, 585.
- [7] K. Fuchs, *Math. Phys. Sci.* **1936**, 153, 622.
- [8] R. Coldwell-Horsfall, A. Maradudin, *J. Math. Phys.* **1960**, 1(5), 395.
- [9] W. Carr, *Phys. Rev.* **1961**, 122(5), 1437.
- [10] S. Brush, H. Sahlin, E. Teller, *J. Chem. Phys.* **1966**, 45(6), 2102.
- [11] T. Engstrom, N. Yoder, V. Crespi, *Astrophys. J.* **2016**, 818(2), 183.
- [12] N. Chamel, A. Fantina, *Phys. Rev. C* **2016**, 94(6), 065802.
- [13] N. Chamel, *J. Phys. Conf. Ser.* **2017**, 932, 012039.
- [14] A. Kozhberov, D. Baiko, *Contrib. Plasma Phys.* **2012**, 52(2), 153.
- [15] A. Kozhberov, D. Baiko, *Phys. Plasmas* **2015**, 22(9), 092903.
- [16] L. Foldy, *Phys. Rev. B* **1978**, 17(12), 4889.
- [17] I. Zucker, *J. Phys. Condens. Matter* **1991**, 3(15), 2595.
- [18] E. Lieb, H. Narnhofer, *J. Stat. Phys.* **1975**, 12(4), 291.
- [19] A. Baldereschi, G. Senatore, I. Oriani, *Solid State Commun.* **1992**, 81(1), 21.
- [20] D. Baiko, A. Potekhin, D. Yakovlev, *Phys. Rev. E* **2001**, 64, 057402.
- [21] D. Kobayakov, C. Pethick, *Phys. Rev. Lett.* **2014**, 112(11), 112504.
- [22] T. Nagai, H. Fukuyama, *J. Phys. Soc. Japan* **1983**, 52(1), 44.
- [23] A. Kozhberov, *Phys. Rev. E* **2018**, 98(6), 063205.
- [24] D. Baiko, A. Kozhberov, *Mon. Not. R. Astron. Soc.* **2017**, 470(1), 517.
- [25] A. Kozhberov, The Structure and Thermodynamic Properties of Coulomb Crystals in the Envelopes of Degenerate Stars (in Russian), Ioffe Institute, Saint Petersburg **2018**.
- [26] D. Baiko, *Phys. Rev. E* **2002**, 66(5), 056405.
- [27] R. Farouki, S. Hamaguchi, *Phys. Rev. E* **1993**, 47(6), 4330.
- [28] S. Hamaguchi, R. Farouki, *J. Chem. Phys.* **1994**, 101(11), 9876.
- [29] R. Farouki, S. Hamaguchi, *J. Chem. Phys.* **1994**, 101(11), 9885.
- [30] S. Hamaguchi, R. Farouki, D. Dubin, *Phys. Rev. E* **1997**, 56(4), 4671.
- [31] A. Kozhberov, *Astrophys. Space Sci.* **2016**, 361(8), 256.
- [32] F. Dyson, *Ann. Phys.* **1971**, 63(1), 1.
- [33] C. Jog, R. Smith, *Astrophys. J.* **1982**, 253, 839.
- [34] S. Ogata, H. Iyetomi, S. Ichimaru, H. van Horn, *Phys. Rev. E* **1993**, 48(2), 1344.

- [35] T. Igarashi, N. Nakao, H. Iyetomi, *Contrib. Plasma Phys.* **2001**, 41(4), 319.
- [36] A. Kozhberov, *Mon. Not. R. Astron. Soc.* **2019**, 486(4), 4473.
- [37] M. Born, *Proc. Camb. Philos. Soc.* **1940**, 36(2), 160.
- [38] G. Kalman, Z. Donko, P. Hartmann, K. Golden, *Europhys. Lett.* **2014**, 107(3), 35001.
- [39] T. Igarashi, H. Iyetomi, *J. Phys. A Math. Theor.* **2003**, 36(22), 6197.

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