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Electrostatic stability of Wigner and Wigner-Dyson lattices

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The local electrostatic stability against homogeneous deformations of uniformly charge-compensated lattices of point charges of the Wigner (unary or single charge species) and Dyson (binary or two charge species in equal concentration) types is explored. Within the scope of these calculations only the bcc, fcc, and hcp unary lattices are found to be locally stable with the bcc having the lowest energy of the three. Among binary lattices, locally stable lattices at various charge ratios of the two species are found to be the CsCl, NaCl, sphalerite (ZnS), tungsten carbide (WC), and the 1:1 gold-copper (AuCu). At very large charge ratio a lattice here dubbed almost bcc is found to be locally and possibly globally stable. Parameters and energies for the above lattices plus that of some locally unstable lattices are given as well as the energies of segregated unary lattices of the two species for all values of the charge ratio. This allows the most-stable lattice at each charge ratio to be determined. It is further conjectured that among binary lattices with a basis of more than two atoms, the wurtzite (ZnS) structure is probably also locally stable over some charge-ratio range. No simple correlation between structure and electrostatic energy has become apparent, but the energies of all locally stable forms differ by 0.1% or less. Some implications are briefly discussed.

I. INTRODUCTION

The concept of a simplified model for solid matter consisting of charged point particles free to move in a uniform background of charge (now often called the "jellium" model) was introduced into physics by Wigner[1] more than forty years ago. He used it as a basis for estimating electron correlation energies in metals, but the model has proved useful in other contexts, and interest in it both from application to new physical situations (such as white dwarf stars and the crusts of pulsars) and as a theoretical model for studying some aspects of conventional matter has continued and grown. The recent appearance of an excellent review of "jellium" models by Care and March[2] makes an extensive discussion of most of these matters unnecessary. But even for this simplest of models of condensed material, many basic questions remain unanswered. In this publication, we shall limit our attention to the stability of Wigner and Wigner-Dyson[3] lattices to homogeneous lattice deformations. We consider only sufficiently low temperatures and densities such that statistics are presumably irrelevant and assume further that the charged particles are spinless (or at least have no spin-dependent interactions). Stability under a homogeneous deformation can here be taken as meaning that the lattice modes for the wave vectors $\vec{k} \to 0$ are stable (have real frequencies) for all directions of $\vec{k}$.

It is useful to make a few remarks about the state of our knowledge in even this simplest regime. Wigner originally proposed that at sufficiently low density, the particles (all presumed to have the same charge) could be sufficiently well localized at such small expense in zero-point energy that the total energy in the ground state was dominated by the classical electrostatic or Coulomb interactions between particles and between particles and the oppositely charged background. Under these conditions one would expect the particles to assume the geometrical configuration of minimum energy and for an infinite system this would be expected to be a simple lattice. Some calculations by Fuchs[4] indicated that among some of the simpler lattices [simple cubic (sc), bcc, fcc] the bcc lattice had the lowest energy. It has been accepted as reasonable by most authors that this is the globally stable state of the system. It is not beyond question, however, that it could be also an amorphous solid or a "complicated" lattice—that is, one having many "atoms" in its basis. We shall here proceed under the assumption that it is a lattice with no more than two "atoms" to the basis.

One should remark further that even at this elementary level one has two types of stability to deal with: local stability, that is, stability with respect to small homogeneous deformations, and global stability or the determination of the structure which has the absolute minimum in energy of the various local minima. We shall not deal here with the question of quantum corrections to the electrostatic energy (zero-point vibrational energy) which become important at increasing density even at the absolute zero of temperature nor thermodynamic stability associated with the effect of finite temperatures and the minimization of the *free* energy of the system.

It is convenient also to introduce some terminology. We shall call a system (or lattice) in which all particles[5] ("atoms") have the same charge a "unary" system, and one in which there are particles of two different charges a "binary" system, distinguishing the two types of particles ("atoms") as "species." We shall not go beyond binary systems here and even in the binary case will restrict ourselves to the case where the concentrations of the two species are equal. We shall use standard terminology for *primitive translation vectors* of the lattice, *Bravais lattices*, and the *basis* of a lattice. Our considerations will be limited to lattices with one or two atoms to the basis. We shall restrict the use of the term *unit cell* to the parallelopiped associated with a set of primitive translation vectors unless otherwise indicated. We shall write for the charge on a particle in a unary lattice Ze and for the charges in a binary lattice Z_1e, and Z_2e, and in this case define $Z = \frac{1}{2}(Z_1 + Z_2)$ so that Ze is always the average charge *per particle*. We shall also define

$$f_1 = Z_1/(Z_1 + Z_2)\ , \quad f_2 = Z_2/(Z_1 + Z_2)$$

as the fractions of charge carried by each particle species. The volume per particle (irrespective of species) will be designated by

$$\tfrac{4}{3}\pi r_s^3 \ .$$

Thus, a "binary" lattice in the limit $f = 0.5$ (identical charges for both species) will have the same energy as a unary lattice with the same charge per particle. The electrostatic energy takes the general form

$$E = -\tfrac{1}{2}aZ^2e^2/r_s$$

or, if r_s is measured in Bohr radii,[6] $me^4/\hbar^2$, and E in atomic units (a.u.)

$$E^{(\text{a.u.})} = -Z^2a/2r_s$$

or with E in Rydbergs

$$E^{(\text{Ry})} = -Z^2a/r_s \ .$$

The numerical constant a for various lattices is the object of the calculations below.

Questions which then need examination and are discussed below on the basis of computer calculations are: (i) Is the bcc lattice indeed the unary lattice of lowest electrostatic energy? (ii) What are the *other* locally stable unary lattices? (iii) For binary lattices of equal numbers of two species, which lattices are locally stable for each value of f, which has the lowest energy, and for the same f, does a segregated mixture of two lattices each composed of one species have a still lower energy? This tells us for each f which situation is likely to be globally stable.

We present below what results we have been able to obtain as a result of computer calculations based on three computer programs: (a) a program to calculate electrostatic energies by Fuch's method[4] for unary and binary lattices; (b) a minimization program of substantial flexibility which could search out points which were potentially local minima of the electrostatic energy in the five-parameter or eight-parameter space of homogeneous deformations for unary and binary lattices, respectively, and (c) a program which could verify whether or not such points found by (b) were relative minima or saddle points and hence could establish (within limits) whether these points were indeed locally stable.

II. CALCULATIONS FOR UNARY LATTICES

Our first results deal with unary (single-species) lattices. We began with Bravais lattices (one "atom" in basis) of higher symmetry (bcc, fcc, sc), calculated the energy constant a, and checked the local stability of the lattice. Then passing to lattices with two "atoms" in the basis, we did the same for more familiar symmetric lattices of this type (hcp and diamond). These were followed by searches for other local minima using the minimum search program and starting from randomly selected initial lattices. All such searches terminated only in either a bcc, fcc, or hcp lattice. None of the results obtained were unexpected except possibly for the fact that the locally stable hcp lattice does not have the ideal c/a ratio, namely, $(c/a)_{\text{ideal}}$, $= (\frac{8}{3})^{1/2}$, but instead the value $c/a = 1.0016(c/a)_{\text{ideal}}$, which is remarkably close to ideal but definitely different.

The results for the energies of the locally stable lattices as well as for some which are of interest though not locally stable are given in Table I. We believe the error in the energies to be no

TABLE I. Energy constants for various unary lattices.

Lattice	Energy constant	
Locally stable lattices:		
Body centered cubic (bcc)	a_{bcc}	$= -1.791\,858\,52$
Face centered cubic (fcc)	a_{fcc}	$= -1.791\,747\,23$
Hexagonal close packed (hcp)[a]	a_{hcp}	$= -1.791\,676\,90$
Locally unstable lattices:		
Simple cubic (sc)	a_{sc}	$= -1.760\,118\,90$
Diamond (dmnd)	a_{dmnd}	$= -1.670\,851\,41$
Almost bcc [abcc($\frac{1}{2}$)], $f = 0.5$	$a_{\text{abcc}(1/2)}$	$= -1.698\,805\,24$
Ideal hexagonal close packed (ihcp)[b]	a_{ihcp}	$= -1.791\,676\,24$

[a] $c/a = 1.001\,6\,(c/a)_{\text{ideal}}$, $(c/a)_{\text{ideal}} = (\frac{8}{3})^{1/2}$.

[b] $c/a = (c/a)_{\text{ideal}}$.

greater than two units in the last quoted digit in each case. The results are in agreement with those of Fuchs[4] for the bcc and fcc lattices, with that of Carr[7] for the sc lattice, and that of Kohn and Schecter[8] for the hcp lattice. An earlier calculation of Herring and Hill[9] indicated that the minimum energy for the hcp lattice occurred at a c/a ratio close to ideal. The programs which we employed can be used with values for f outside the range $(0, 1)$ to determine the Madelung energy of ionic lattices. Our results are in agreement with the very accurate Madelung constants of Sakamoto[10] for the NaCl, CsCl, and ZnS lattices, but not quite so precise.

We emphasize that we have not sought to find stable lattices which have more than two "atoms" per unit cell. Our programs would also have missed a very shallow relative minimum or one of small extent in parameter space with one or two atoms per unit cell.

III. CALCULATIONS FOR BINARY LATTICES

In view of the possible astrophysical significance of binary (Wigner-Dyson)[11] Coulomb lattices we have attempted a fairly comprehensive search for such lattices with local stability against homogeneous deformations and as a result obtain significant information about the likely global symmetry for all values of the charge-ratio parameter f (defined earlier) from $f = 0.5$ (equal charged species) to $f = 1$ (one species neutral). The results for $0 < f < 0.5$ are, of course, identical with those for $f = 1 - f$ while for f negative, the species have opposite sign and the lattice would certainly be (electrostatically) unstable.

In the case of binary lattices, one can use simple arguments to suggest the existence or range of local stability as a function of f for various lattices. We outline these arguments below and eventually present the totality of available results.

(a) Consider the binary CsCl lattice, which has two atoms per unit cell. If $f = 0.5$ all atoms have the same charge, the lattice becomes a bcc lattice and we know this to be locally (and probably, globally) stable. On the other hand, if $f = 1.0$, from the electrostatic point of view, the lattice becomes an sc lattice which we know to be locally unstable. Hence, as we increase f from 0.5 to 1.0, we must pass a critical value of f at which the CsCl lattice becomes locally unstable. We find this value to lie in the neighborhood of $f = 0.8621$.

(b) Consider an NaCl lattice for $f = 1.0$ in which case it is electrostatically an fcc lattice and therefore locally stable. As f decreases to $f = 0.5$, it becomes a unary sc lattice which is locally unstable. Hence, there is a critical value of f in this range below which local instability of the NaCl lattice sets in. We find the value to be in the neighborhood of $f = 0.7545$.

(c) Let us now return to the fcc lattice and consider the smallest *cubical* cell (which contains two "atoms") with, say, A atoms at the corners and at the centers of all the faces. Now replace the center atoms on the side faces of the cube by B atoms but keep A atoms at the centers of the top and bottom faces of the cube. We then have a binary lattice whose primitive translation vectors extend from, say, from one lower corner atom to an adjacent lower corner atom, to the face-centered atom at the base, and to the corner atom directly above. The second vector of the basis may then be selected to be that from the same corner atom to one of the side face-centered atoms. Clearly if the A and B atoms are different, the cubical symmetry is destroyed and the lattice becomes tetragonal. We shall call this lattice AuCu [Wyckoff[12] RX type AuCu (j)]. When $f = 0.5$ it degenerates to a simple fcc lattice. As f increases to unity one would come back to an sc lattice in this limit. Thus, again there is a critical value of f at which the lattice becomes locally unstable. What actually happens is that as f increases from 0.5 to about 0.528 the stable c/a ratio decreases steadily from 1.0 to about 0.95; as f increases further the c/a ratio drops suddenly to $2^{-1/2}$ for which value the lattice is actually a CsCl lattice. As indicated earlier this lattice

TABLE II. Energy constants for WC and AuCu lattices.

Lattice	f	c/a		Energy constant a
WC	0.50	1.0016	$(c/a)_{\text{ideal}}$[a]	−1.791 676 91
	0.52	0.9973	$(c/a)_{\text{ideal}}$	−1.792 770 65
	0.54	0.9846	$(c/a)_{\text{ideal}}$	−1.796 107 15
	0.56	0.9640	$(c/a)_{\text{ideal}}$	−1.801 845 67
	0.58	0.9364	$(c/a)_{\text{ideal}}$	−1.810 230 87
	0.60	0.9028	$(c/a)_{\text{ideal}}$	−1.821 564 11
	0.615[b]	0.8910	$(c/a)_{\text{ideal}}$	−1.832 120 24
AuCu	0.500	1.0000	$(c/a)_{\text{ideal}}$	−1.791 858 52
	0.505	0.9986	$(c/a)_{\text{ideal}}$	−1.791 835 40
	0.510	0.9946	$(c/a)_{\text{ideal}}$	−1.792 100 49
	0.515	0.9871	$(c/a)_{\text{ideal}}$	−1.792 544 39
	0.520	0.9754	$(c/a)_{\text{ideal}}$	−1.793 170 55
	0.525	0.9552	$(c/a)_{\text{ideal}}$	−1.793 985 14
	0.520[b]	0.9504	$(c/a)_{\text{ideal}}$	−1.795 466 27

[a] $(c/a)_{\text{ideal}} = (\frac{8}{3})^{1/2}$.

[b] Approximate limit of local stability.

then remains stable until f reaches 0.8621. A table of energy constants a_{AuCu} and the locally stable c/a ratio of AuCu lattices is given in Table II over the range of local stability.

(d) Let us now consider a bcc lattice of atoms of species A. Suppose that we introduce one atom of species B in the unit cell but that the charge of species B is much smaller than that of species A. Thus, the presence of B's would have small influence on the positions of the A's, but the B atoms would seek out positions which minimize locally the electrostatic energy; i.e., the positions of lowest electrostatic potential in the A lattice.

A stable point is found for B's of very small charge where the B's lie in the face of the bcc cubic cell one-quarter of the way across the face on a line lying midway between two parallel edges of that face. This arrangement leads to a (nonregular) tetrahedral arrangement of the nearest neighbors of each particle, but this lattice is locally stable[13] only in the narrow range $0.9993 \leq f \leq 1.0$. We have dubbed this lattice simply "almost bcc" or abcc. Incidentally, this approach applied to the fcc lattice yields the NaCl lattice which was explored earlier. But it yields also the zinc-blende or sphalerite ZnS structure stable from $f = 0.9625 \pm 0.0005$ to $f = 1.0$. We designate the zinc-blende structure simply as ZnS.

(e) Finally, we consider the hcp lattices. In the unary case this is not a Bravais lattice so the change to a binary lattice consists in making the second basis "atom" of the lattice a B atom. Wyckoff[12] uses the nomenclature tungsten carbide or WC [also WC (z)] for this lattice. This is locally stable at $f = 0.5$ with $c/a = 1.0016(c/a)_{\mathrm{ideal}}$, where $(c/a)_{\mathrm{ideal}} = (\frac{8}{3})^{1/3}$ but as f increases become unstable at a critical value of f in the range $0.615 \leq f \leq 0.616$. At the same time, c/a decreases to $0.873(c/a)_{\mathrm{ideal}}$. Numerical values are given in Table II.

(f) It is now relevant to speak of other possible locally stable binary lattices of the type we have been considering but whose existence cannot be inferred from the general arguments as above. Here we have again used a minimum search program starting from randomly selected points in the parameter space of lattices with two atoms in the basis with $f = 0.6$, 0.7, 0.8, and 0.9. These are long searches since the parameter space is eight dimensional. We found no new lattices in this way and in the overwhelming number of cases the search ended in either NaCl or a CsCl lattice and very occasionally in the WC lattice. In our necessarily limited numbers of searches made only for f values differing by 0.1, we did not reach any of the more esoteric lattices such as the ZnS, abcc, or AuCu. We would certainly have missed lattices with very limited stability ranges either in f or, for given f, in the parameter space. It is reasonable to conjecture, however, that among binary lattices with a larger basis than two atoms, the wurtzite lattice is likely to be locally stable in the range just below $f = 1.0$.

(g) The last possibility we must consider for binary lattices, as Dyson pointed out in his original discussion,[3] is that with two species it is possible that the lowest energy of the system may be realized by segregation of the two species with each crystallizing in the lowest-energy unary lattice, presumably bcc. In fact, it will be useful to use the energy of such a segregated bcc-bcc system as a function of the charge parameter f as a base line from which to measure the values of the energy parameter a for all lattices. As Dyson showed, for two unary lattices with charges Z_i and Z_j and with $Z = \frac{1}{2}(Z_i + Z_j)$ the energy of the two segregated lattices will be given by the energy constant[3]

$$a_{\mathrm{seg}}(i,j) = \tfrac{1}{2}[a_i(2f)^{5/3} + a_j(2-2f)^{5/3}] \tag{1}$$

Thus, with the choice $a_i = a_j = a_{\mathrm{bcc}}$ we obtain this reference energy constant which is plotted as a function of f in Fig. 1. The same formula can be used for the other segregated lattice situations, but it should be noted that for two different lattices (such as bcc and hcp), the constant a will depend on which of the two species forms which lattice. We shall write the energy constants in these segregated cases in the form $a_{\mathrm{seg}}(i,j)$ where i is the lattice formed by the species of *higher* charge and j that of *lower* charge. (It is in this manner that they are designated in Fig. 4 where i and j run over bcc, fcc, and hcp.)

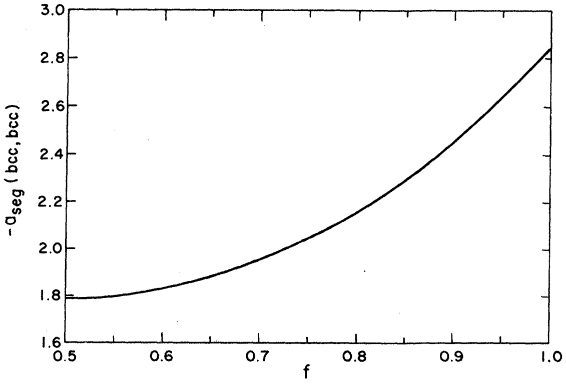

FIG. 1. Coulomb energy constant a_{seg}(bcc, bcc) for two segregated lattices consisting of two species with unequal charges (except at $f = 0.5$) each crystallized in a bcc lattice. Accurate values may be calculated from Eq. (1) in conjunction with Table I; in this case $a_i = a_j = a_{\mathrm{bcc}}$.

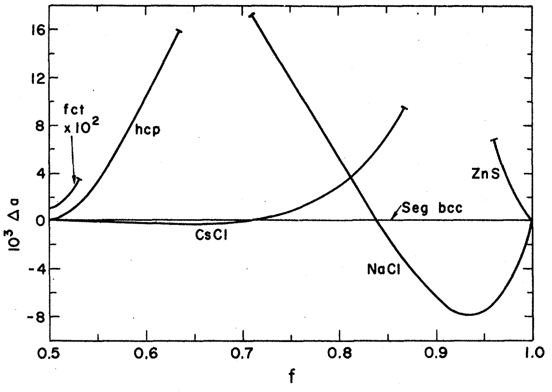

FIG. 2. Difference in Coulomb energy constants $\Delta a = a - a_{\mathrm{seg}}(\mathrm{bcc,bcc})$ for locally stable lattices over their range of local stability. The CsCl lattice appears to be the globally stable lattice from $f = 0.5$ to $f \simeq 0.7076$; the segregated bcc-bcc lattice is then apparently globally stable from 0.7076 to $f \simeq 0.8386$, at which point the NaCl lattice appears to become the globally stable lattice almost to $f = 1.0$. There the lattice we have called abcc is more stable (see Fig. 3). The cross bars show the limits of *local* stability for each lattice.

IV. RESULTS

For those interpenetrating Bravais lattices whose configurations do not change with f such as CsCl, NaCl, ZnS (zinc blende), and abcc, the energy for each value of f can be calculated by the formulas:

$$\begin{aligned} a_{\mathrm{CsCl}} &= a_{\mathrm{bcc}} + 4(4^{1/3}a_{\mathrm{sc}} - a_{\mathrm{bcc}})(f - \tfrac{1}{2})^2 ,\\ a_{\mathrm{NaCl}} &= a_{\mathrm{sc}} + 4(4^{1/3}a_{\mathrm{fcc}} - a_{\mathrm{sc}})(f - \tfrac{1}{2})^2 ,\\ a_{\mathrm{ZnS}} &= a_{\mathrm{dmnd}} + 4(4^{1/3}a_{\mathrm{fcc}} - a_{\mathrm{dmnd}})(f - \tfrac{1}{2})^2 ,\\ a_{\mathrm{abcc}}(f) &= a_{\mathrm{abcc}}(\tfrac{1}{2}) + 4[4^{1/3}a_{\mathrm{bcc}} - a_{\mathrm{abcc}}(\tfrac{1}{2})]\,(f - \tfrac{1}{2})^2 . \end{aligned} \tag{2}$$

The energy constants a_{bcc}, a_{sc}, a_{fcc}, a_{dmnd}, and $a_{\mathrm{abcc}}(\frac{1}{2})$ are given in Table I. For the AuCu and WC lattices, the configuration of the stable lattice changes with f and such simple formulas are not available. For this reason the energy constants together with the c/a ratios for these binary lattices are given in Table II.

In Fig. 2, we have plotted the energy constants of the various locally stable binary lattices over their range of local stability relative to the energy constant $a_{\mathrm{seg}}(\mathrm{bcc,\ bcc})$. From this figure, we can see which of the lattices we have explored is possibly the globally stable lattice for each value of the charge ratio f. The region of this graph where $f \simeq 1$ is shown on an expanded scale in Fig. 3 so that details can be observed. Even in this figure in the region where the abcc lattice is apparently globally stable, its difference from the segregated (bcc, bcc) lattice is too small to be discriminated, the difference being of order 2×10^{-5}. Finally, in Fig. 4 we show the energy constants of the various segregated, locally stable lattice combinations plotted with the baseline again given by $a_{\mathrm{seg}}(\mathrm{bcc,\ bcc})$.

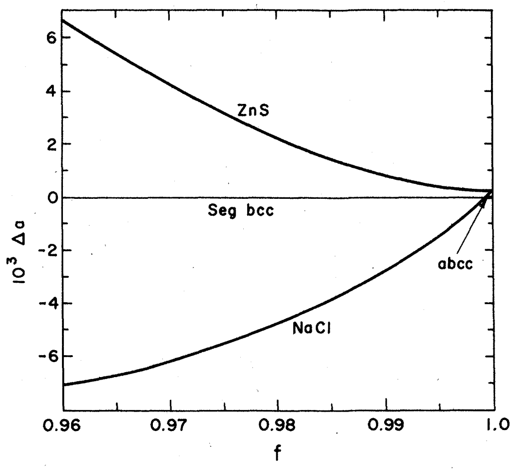

FIG. 3. Magnified view of the region about $f = 1.0$ in Fig. 2. The abcc lattice although slightly lower in energy, coincides with the $a_{\mathrm{seg}}(\mathrm{bcc,bcc})$ curve to the accuracy of the figure from about the point where the latter crosses the NaCl curve.

V. SUMMARY

In general, no surprising results have emerged from this study. One finds that energy differences for locally stable lattices at any f value are quite small, of the order of one part in 10^3. For the global stability of binary lattices, the general stability results confirm the results of Dyson except for a physically uninteresting region in a very small neighborhood about $f = 1.0$, in spite of the

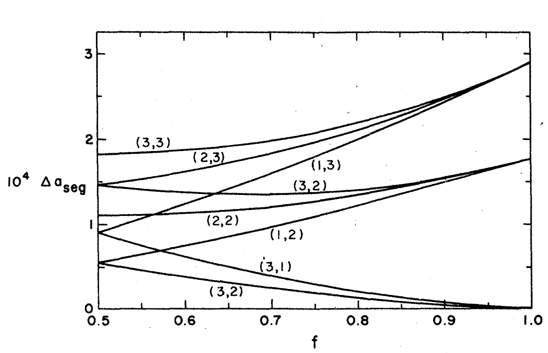

FIG. 4. Difference $\Delta a_{\mathrm{seg}}(i,j) = a_{\mathrm{seg}}(i,j) - a_{\mathrm{seg}}(1,1)$ where i, $j = 1$, 2, and 3, respectively, stand for the bcc, fcc, and hcp lattices. The first figure in parentheses represents the lattice of the species of higher charge, the second representing the lattice of the species of lower charge. The lowest curve should be labeled (2,1) rather than (3,2). The baseline is (1,1) = (bcc,bcc).

fact that we have uncovered five more locally stable lattices than were considered by Dyson. It also seems to be very difficult to understand the pattern of correlation between energy and lattice structure. This combined with the smallness of energy differences of locally stable lattices, suggests that in the density regime where the Wigner lattice structure is valid in the electrostatic limit, the presence of even relatively small numbers of other charge impurities may have major effects on the lattice structure in their neighborhood (or within the radius of the Debye screening length when the background charge is a degenerate electron gas.) Further stability questions with respect to the effect of lattice vibrations will be explored in a later publication.

Note added in proof. The NaCl curve in Fig. 2 should terminate with a cross bar at $f = 0.755$ rather than 0.71.

ACKNOWLEDGMENTS

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[1] E. P. Wigner, Phys. Rev. 46, 1002 (1934); Trans. Faraday Soc. 34, 678 (1938).

[2] C. M. Care and N. H. March, Adv. Phys. 24, 101 (1975).

[3] F. J. Dyson, Ann. Phys. (N.Y.) 63, 1 (1971).

[4] K. Fuchs, Proc. R. Soc. London A 151, 585 (1935).

[5] The terms "particles" and "atoms" are used interchangeably in the present manuscript. In the context of electron-gas correlation, the terms have reference to the electrons; in the case of white dwarfs or pulsars, they refer to the nuclei with a degenerate electron gas playing the role of the background electron charge.

[6] The term "Bohr radius" is used here irrespective of whether m is the electron or some other mass.

[7] W. J. Carr, Jr., Phys. Rev. 122, 1437 (1961).

[8] See footnote 10 in Ref. 7.

[9] C. Herring and A. G. Hill, Phys. Rev. 58, 132 (1940).

[10] Y. Sakamoto, J. Chem. Phys. 28, 164 (1958).

[11] See Ref. 3 and T. A. Witten, Jr., Astrophys. J. 188, 615 (1974) as well as references in these papers and in Ref. 2.

[12] W. C Wyckoff, *The Structure of Crystals*, 2nd ed. (Reinhold, New York, 1931).

[13] Actually it is not possible for us to determine within the limits of our accuracy whether this is a cubic structure or whether there is a very small deformation associated with the introduction of the second ion of very small charge.