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Phase Transition in a Wigner Lattice*

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Detailed calculations of the frequency spectrum of lattice vibrations for the body-centered-cubic and face-centered-cubic Wigner lattices in the harmonic approximation show that a phase transition from the body-centered-cubic to either the face-centered-cubic lattice or to some other lattice almost certainly occurs with increasing temperature at sufficiently low densities, but a transition from the body-centered-cubic to the face-centered-cubic lattice does not occur at zero temperature with increasing density in the region where the harmonic approximation is valid. The parameterless frequency spectra for the two lattices, which have been calculated to relatively high accuracy, and their moments are tabulated.

I. INTRODUCTION

The problem of a many-body system consisting of identical point-charged particles moving in a compensating rigid uniform background of opposite charge was first studied as a model for the electron gas in a solid. At zero temperature (or sufficiently low temperatures) and very high densities, the system behaves as a degenerate Fermi gas, and hence is a fluid. In the high-density expansion of the zero-temperature energy of such a system, the leading terms are the Fermi energy and the exchange energy associated with the Coulomb interaction. The next two terms in the expansion were first obtained by Gell-Mann and Brueckner[1] and are the leading terms in what is called the correlation energy of the system. An early attempt to estimate the correlation energy of the electron gas, particularly at intermediate densities, led Wigner[2] to examine the low-density limit of the same system and to discover that in this limit such a system (whether composed of fermions or bosons) crystallizes in the classical configuration of minimum potential energy which, by all indications, appears to be a body-centered-cubic (bcc) lattice. Thus, as a function of density, even at zero temperature, a fermion system of this type must undergo a phase transition from a crystalline to a fluid phase. A similar situation seems to prevail for boson systems at zero temperature since the high-density behavior is predicted to be that of a superfluid.[3] Furthermore, the elementary excitations of the high-density boson system appear to be plasma oscillations (plasmons) with a finite energy gap separating them from the ground state, while the low-energy excitations of the low-density Wigner lattice are phonons with no energy gap. Thus there must be a transition density at which the finite gap disappears.

Since Wigner's original exploration of the so-

called Wigner lattice, there have been extensive further studies of the low-density limit.[4-8] While originally these explorations for both boson and fermion systems were primarily of academic interest, it has subsequently developed that they may be relevant to certain astrophysical situations.[9] Furthermore, such charged-particle systems represent fertile models for obtaining insight into the real behavior of many-body systems which show a fluid-solid transition. In this respect they share a powerful advantage with the hard-sphere system over all other such models in that when the density and temperature are expressed in suitable reduced units there are no free parameters in the problem.

While several investigations have been attempted of the fluid-solid transition,[10] no conclusive results have so far been obtained. There is another question, however, to which a definitive answer has been lacking, and it was the desire to obtain a conclusive answer to it which prompted the present investigation. This question is: Does a transition from the bcc Wigner lattice to another lattice, in particular the face-centered-cubic (fcc) lattice, take place with either increasing density or temperature in the region in which the harmonic approximation for the treatment of lattice vibrations is valid? This question is prompted by the fact that the Coulomb potential energy (per particle) in these two lattices, and in the hexagonal close-packed (hcp) lattice as well, differs only by a few parts in ten-thousand[11,12]:

$$V_0 = a r_s^{-1} , \qquad a(\text{bcc}) = -1.791\,860 ,$$

$$a(\text{fcc}) = -1.791\,753 , \quad a(\text{hcp}) = -1.791\,68 ,$$

where r_s is the usual parameter, defined below, which measures the density of the system. Thus even small energy differences associated with the zero-point or thermal energy of oscillation of these lattices could induce a transition at increasing density or temperature. While earlier calculations for the bcc and fcc lattices have been performed, they have not been of sufficient accuracy to give a definitive answer to this question. Thus though no new theoretical ideas are introduced in the present work, the results of calculations of adequate precision to answer this question and incidentally to detail some other features of interest of these Wigner lattices are presented. In particular, the following features of the bcc and fcc lattices are discussed:

(a) the frequency spectrum of normal modes of both lattices being determined to a much higher precision than these completely parameterless spectral distributions have ever been determined before, and, to our knowledge, are the only ones to be published;

(b) strong evidence for the absolute stability of both the bcc and fcc lattices against all small deformations;

(c) the incidental determination of a large number of moments of the frequency spectra for the lattices;

(d) determination of the low-temperature, low-density specific heat, internal energy, and free energy of the two lattices. It is thereby found that a coexistence curve is possible in the region of validity of the harmonic approximation for the two lattices. Whether or not a direct transition between these two specific lattices actually occurs will then depend on whether still another lattice type becomes more stable in a region which completely covers this coexistence curve, but it appears certain that some lattice transformation must occur with increasing temperature in the low-density region.

II. NOTATION

We shall use the following notation which is more or less standard for this problem: We let n represent the number density of charged particles of mass m and charge e. The radius r of the spherical volume per particle is then defined by

$$\tfrac{4}{3}\pi r^3 = 1/n .$$

The relevant "Bohr radius" for the system is defined by

$$a_0 = \hbar^2/me^2 .$$

The dimensionless parameter r_s which measures the density of the system is then defined by

$$r_s = \frac{r}{a_0} = \left(\frac{3}{4\pi n}\right)^{1/3} \frac{me^2}{\hbar^2} .$$

We use the "rydberg"

$$1\ \text{Ry} = me^4/2\hbar^2$$

as the unit of energy. The plasma frequency ω_p is given by

$$\omega_p = (4\pi ne^2/m)^{1/2} ,$$

and the associated energy is then

$$\hbar\omega_p = 2\sqrt{3} r_s^{-3/2}\ \text{Ry} .$$

We use x for the frequency of a normal mode in units of the plasma frequency ω_p (which is the upper limit of the spectrum):

$$x = \omega/\omega_p .$$

The frequency distribution function of the lattice will be designated by $g(x)$ and normalized to

$$\int_0^1 g(x)\,dx = 1 .$$

The Kohn sum rule for the three frequencies associated with a given wave vector is then

$$x_1^2 + x_2^2 + x_3^2 = 1 .$$

The division between the acoustic and the optic branches of the spectrum occurs at $\omega = \omega_p/\sqrt{3}$ or

$$x = 1/\sqrt{3} = 0.578 .$$

Moments of the frequency distribution u_n are defined by

$$u_n = \int_0^1 x^n g(x)\,dx .$$

We use T to represent the absolute temperature and with k for Boltzmann's constant, define the dimensionless temperature t by

$$t = 2\hbar k T/me^4 ,$$

which is the energy kT in rydbergs. It will also be convenient to introduce another temperature variable τ by

$$\tau = kT/\hbar\omega_p = tr_s^{3/2}/2\sqrt{3} ,$$

which measures the thermal energy relative to the scale of quantum excitation energies of the system.

III. CALCULATION OF NORMAL-MODE FREQUENCIES

The frequency spectra of normal modes of vibration of the bcc and fcc lattices (in the harmonic approximation) were calculated by the determination of normal-mode frequencies at large numbers of points in phase space (wave vectors in the first Brillouin zone in reciprocal-lattice space). The elements of the matrix whose eigenvalues are the squares of the eigenfrequencies were calculated using formulas based on the Ewald's method[13] as listed by Cohen and Keffer.[14] All calculations were programmed for and executed on a PDP 9/L computer associated with the physics department of Case Western Reserve University. The programs were checked against the numerical calculations of Cohen and Keffer and (for the bcc lattice) against the calculated eigenfrequencies listed for special wave vectors by Clark[4] and by Carr.[5] A last, and particularly impressive, check was provided by making use of the fact that the fourth moment of the frequency distribution as obtained from the frequency spectra can be directly related to a certain sum over the direct lattice, namely, the inverse sixth powers of the distance of all lattice points from a given point.[6] The latter have been calculated previously by Ingham and Jones[15] and agree to better than one part in 10^4 with the values we obtain.

The sets of wave vectors for which calculations were performed consisted both of regular arrays in reciprocal-lattice space and of a set of 17 500 randomly chosen independent wave vectors for each lattice in its reciprocal-lattice space. The arrays consisted of rhomboidal arrays of 680, 1540, and 2925 independent vectors, respectively. While the latter provided adequate information to obtain the desired zero-point energy of the lattices, the associated frequency spectra were still quite ragged. It was for this reason that the random sets of many more points were calculated.

For no wave vectors were the squares of the normal-mode frequencies found to be negative for either of the two lattices. This makes it virtually certain that these two lattices are stable against all possible lattice deformations which are sufficiently small in magnitude for the harmonic approximation to apply.

IV. FREQUENCY SPECTRA AND MOMENTS

The three frequencies associated with each of the 17 500 randomly selected wave vectors provide one with a rather detailed frequency distribution function or spectrum of normal modes for each lattice. This function, together with a computer-generated histogram of the distribution is presented in Fig. 1 for the bcc lattice and in Fig. 2 for the fcc lattice. The vertical column of numbers from 1 to 50 at the left of each figure label the 50 bins of width 0.02 in the frequency variable $x = \omega/\omega_p$. The numbers of the right give the spectral distribution function $g(x)$ evaluated at $x = 0.01, 0.03, \ldots, 0.97, 0.99$, respectively. The accuracy of these figures is estimated at about $\sqrt{g}/30$ both statistically and as judged by the convergence as additional values were calculated.

The general similarity of the two spectra is owing in part to the well-known division of the frequency spectrum into two parts, the "acoustical" spectrum lying below $x = 1/\sqrt{3} = 0.578$ and the "optical" spectrum lying above this point. This point occurs in bin 29. The principal differences in the spectra are the sharp peak in the bcc spectrum in bin 12 and the more rapid filling in of the optical spectrum for the fcc lattice above bin 29.

The extensive frequency calculations also permit the determination of moments of the frequency spectrum to relatively high precision. While the first 100 moments for each spectrum have been calculated, we here present only the first twenty moments for each lattice in Table I. These values are estimated to be accurate to about one part in 10^5 at least. From this fact one is forced to conclude that the values for s_3, s_4, u_6, and u_8 given in Ref. 6 for the bcc lattice are not correct to the accuracy claimed, and that the correct values of s_3 and s_4 are

$$s_3 = 2.0599 \times 10^{-2} ,$$

$$s_4 = 1.6880 \times 10^{-2} .$$

This would bring the values in much closer accord with the corresponding values for the fcc lattice as obtained in Ref. 8; the latter values concur with

those obtained here to the accuracy there claimed.

V. THERMODYNAMIC FUNCTIONS

The zero-point energy in rydbergs per particle associated with the normal modes of vibration of a crystal lattice is expressed in terms of the first moment u_1 of the frequency spectrum by

$$\tfrac{3}{2}\hbar\omega_p u_1 = 3\sqrt{3}\, u_1 r_s^{-3/2} = b r_s^{-3/2} .$$

From the values of u_1 in Table I, one finds

$$b(\text{bcc}) = 2.659\,02, \quad b(\text{fcc}) = 2.667\,72 .$$

The thermal contribution of the vibrational energy to the Helmholtz free energy per particle F, also in rydbergs per particle, is given by

$$F_{\text{th}} = -2\sqrt{3}\, r_s^{-3/2} h(\tau) ,$$

where

$$h(\tau) = -3\int_0^1 g(x)\ln(1-e^{-x/\tau})\,dx ,$$

with $g(x)$ the frequency spectrum for the appropriate lattice and $\tau = kT/\hbar\omega_p$. The function $h(\tau)$ for the bcc lattice, as well as the difference between

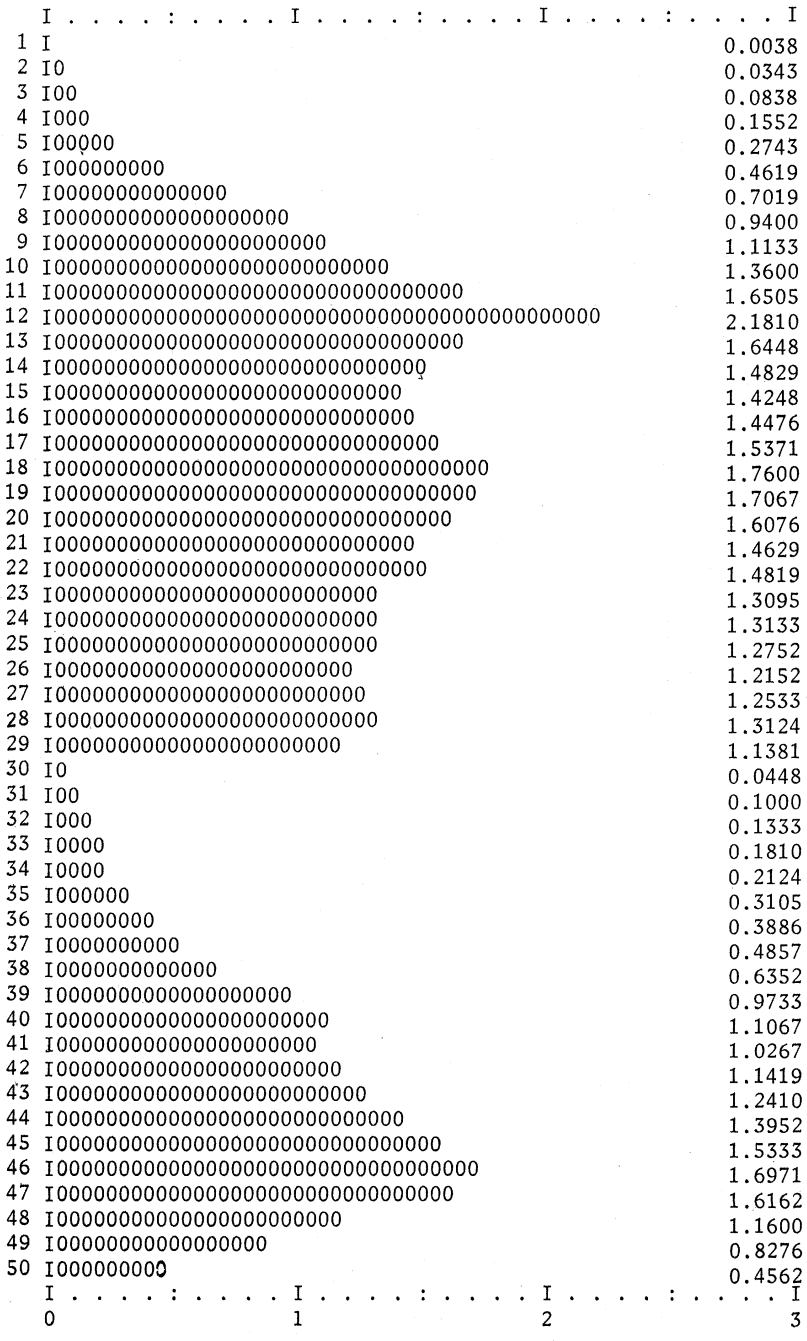

FIG. 1. Histogram of vibrational frequency distribution for the bcc Wigner lattice. Numerals on left number bins of width 0.02 in $x = \omega/\omega_p$. Numbers on right give values of $g(x)$ at $x = 0.01, 0.03, \ldots, 0.99$. Frequency increases going from top to bottom of figure.

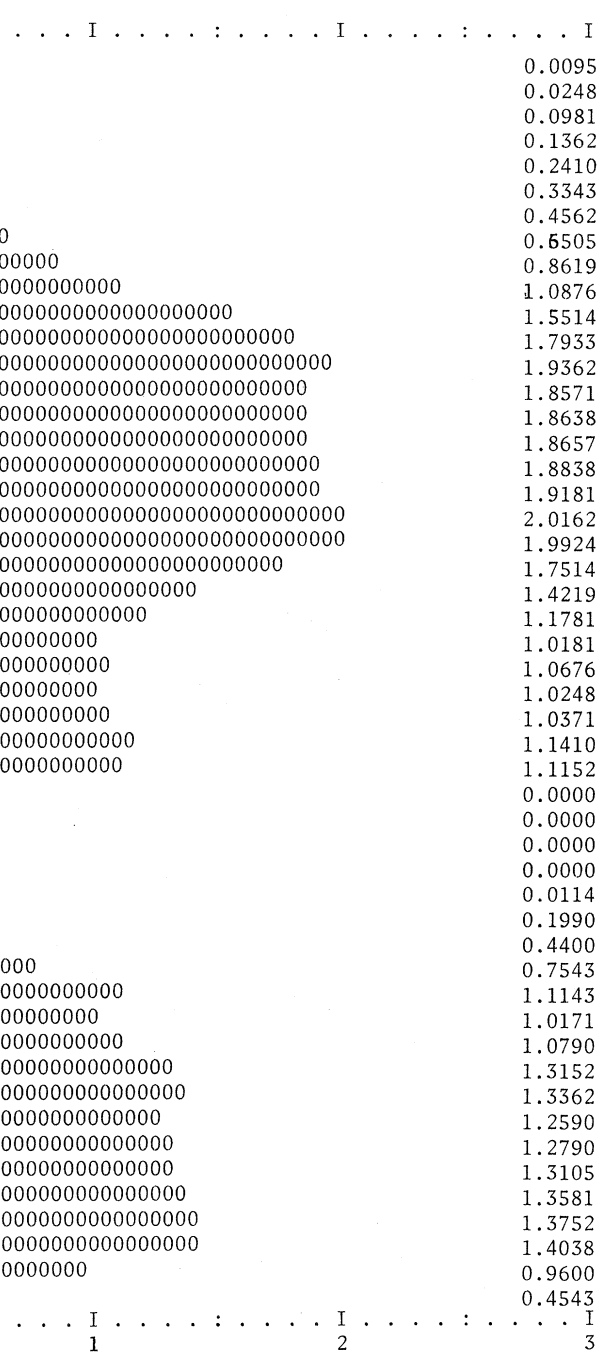

FIG. 2. Histogram of vibrational frequency distribution for fcc Wigner lattice. For interpretation see caption for Fig. 1.

$h(\tau)$ for the bcc and fcc lattices, is plotted as functions of τ in Fig. 3. Thus the total Helmholtz free energy per particle in the harmonic approximation can be expressed for each lattice in the form

$$F(r_s, \tau) = ar_s^{-1} + br_s^{-3/2} - 2\sqrt{3}\, r_s^{-3/2} h(\tau) .$$

From F one may obtain the internal energy $U(r_s, \tau)$ from the formula

$$U = F - \tau\left(\frac{\partial F}{\partial \tau}\right)_{r_s},$$

and from this in turn the specific heat at constant volume is obtained by differentiation with respect to T. At low temperatures, $\tau \ll 1$, this specific heat is determined by the low-frequency behavior of the frequency spectrum:

$$g(x) \to c_2 x^2 ,$$

where the coefficient c_2 can be obtained by averaging the inverse third power of the sound velocity of the long-wavelength modes over all directions in the crystal. Accurate numerical calculations by

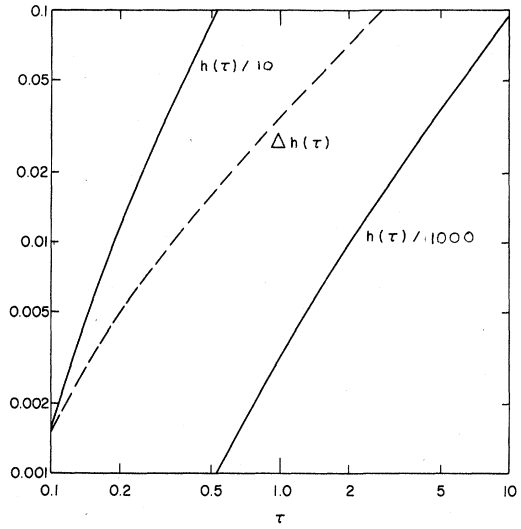

FIG. 3. Solid curves give the function $h(\tau)$ for the bcc crystal lattice. The dashed curve represents $\Delta h(\tau) = h_{\rm bcc}(\tau) - h_{\rm fcc}(\tau)$.

the latter method yield

$$c_2(\text{bcc}) = 32.226\,, \quad c_2(\text{fcc}) = 35.216\,,$$

with an accuracy of better than one part per thousand. The value of c_2(bcc) may be compared with the value 29.98 obtained in Ref. 6 and a value between 31 and 32 obtained in Ref. 5, while c_2(fcc) can be compared with the value 34.8 obtained in Ref. 8. From these one obtains for the specific heat at constant volume per particle

$$C_v = ckr_s^{9/2}t^3 \qquad (t \ll \hbar\omega_p)\,,$$

with k in rydbergs per °K and

$$c(\text{bcc}) = 60.40, \quad c(\text{fcc}) = 66.04.$$

The lattice type which is stable at a given density and temperature is determined by the requirement that F be a minimum. Since we treat, at given density of the system, the background charge as rigid at the appropriate value, it is not possible to have separation and coexistence of the two phases in equilibrium over a range of densities (that is, a range of volumes for fixed total number of particles) for the system.[16] If a phase transition is possible it is then determined by the vanishing of the difference of the free energies for the two systems and the equation for the transition line is given by

$$h(\tau) = (\Delta a r_s^{1/2} + \Delta b)/2\sqrt{3}\,,$$

where

$$\Delta a = a(\text{bcc}) - a(\text{fcc}) = 0.000\,107\,,$$

$$\Delta b = b(\text{bcc}) - b(\text{fcc}) = 0.008\,70\,,$$

$$\Delta h(\tau) = h_{\rm bcc}(\tau) - h_{\rm fcc}(\tau)\,.$$

The quantity $\Delta h(\tau)$ is plotted as a function of τ in Fig. 3. The transition line in the (r_s, τ) plane is shown in Fig. 4 as the full line. Its asymptotic form for large r_s is given by

$$\tau = 0.000\,082\,9 r_s^{1/2}\,.$$

The low-temperature side of the transition line is occupied by the bcc lattice phase, the high-temperature side by the fcc phase. One can easily calculate the latent heat associated with the transition; one finds that for $\tau > 1$ it is given by $1.07 \times 10^{-5} r_s^{-1}$ and hence is always very small.

It will be noted that at the absolute zero of temperature no transition from the bcc to the fcc lattice occurs (in the harmonic approximation) with increasing density. Whether an actual transition from the bcc to the fcc lattice occurs with increasing temperature depends on two conditions being satisfied, however.

(a) A transition from the bcc lattice to some still different lattice does not occur with increasing temperature prior to the transition to the fcc lattice over the entire range of r_s for which the latter transition might occur.

(b) At least part of the transition line lies in a region in which the harmonic approximation is indeed valid. In Sec. VI we attempt to delineate this region.

VI. VALIDITY DOMAIN FOR HARMONIC APPROXIMATION

A reasonable estimate of the region of validity of

TABLE I. Moments of frequency distributions.

n	u_n(bcc)	u_n(fcc)
1	0.511 73	0.513 40
2	0.333 34	0.333 33
3	0.250 23	0.249 78
4	0.203 08	0.202 65
5	0.172 10	0.171 73
6	0.149 60	0.149 25
7	0.132 14	0.131 78
8	0.118 00	0.117 64
9	0.106 23	0.105 89
10	0.096 24	0.095 94
11	0.087 65	0.087 42
12	0.080 19	0.080 05
13	0.073 66	0.073 61
14	0.067 91	0.067 96
15	0.062 81	0.062 96
16	0.058 27	0.058 52
17	0.054 20	0.054 55
18	0.050 55	0.050 99
19	0.047 27	0.047 79
20	0.044 29	0.044 89

the harmonic approximation can be obtained by requiring that the mean-square amplitude for oscillation of a particle about its equilibrium lattice position arising from both zero-point and thermal vibrational energy be small compared to r^2 which is approximately the square of the interparticle spacing. Calling the former $\langle d^2\rangle$, this condition takes the form[6]

$$\frac{\langle d^2\rangle}{r^2}=\left(\frac{3}{r_s}\right)^{1/2}\int_0^1 \frac{g(x)}{x}\coth\frac{x}{2\tau}dx \ll 1 .$$

This integral has been evaluated using the calculated bcc lattice spectrum. The relationships between r_s and τ for values of $\langle d^2\rangle/r^2 = 1$, 10^{-2}, and 10^{-4} are plotted as dashed curves in Fig. 4. It follows from this figure that for $r_s > 10^5$ the actual value of $\langle d^2\rangle/r^2$ is less than 10^{-3} and for large r_s approaches 3×10^{-4}. It would thus appear safe to assume that the bcc-fcc transition line lies within the region of validity of the harmonic approximation almost certainly for $r_s > 10^5$ and very possibly for r_s as small as 10^{-2}. It follows then that again almost certainly *some* phase transition occurs with increasing temperature at densities such that $r_s > 10^5$. The associated transition line can terminate only on some other transition line (or at $\tau = 0$, which does not appear likely). If melting of the lattice occurs when Lindemann's criterion is satisfied, the solid-fluid transition would be along one of the lines of constant $\langle d^2\rangle/r^2$. In this case the solid-solid transition line would presumably terminate on a member of this family of curves.

Note added in proof. After submission of this paper we were informed by Professor A. Maradudin of work of Dr. R. J. Laster (thesis, Southern Methodist University) in which frequency spectra for bcc and fcc Wigner lattices have been calculated. The results are in agreement with those presented above and show that a bcc to fcc transition does not occur at zero temperature. Since behavior at elevated temperatures is not explored, the phase transition is not revealed.

The author also desires to take this opportunity to dedicate this paper to the memory of a distinguished colleague and esteemed friend, the late Professor Leonard I. Schiff.

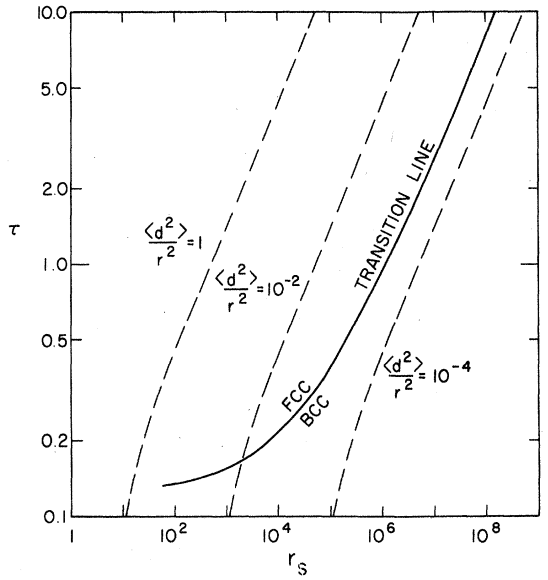

FIG. 4. Solid curve represents the transition line between the bcc and fcc lattices in the (τ, r_s) plane. The fcc lattice is stable above the line, the bcc below. The dashed curves are lines in the (τ, r_s) plane on which $\langle d^2\rangle/r^2$ is constant. The harmonic approximation should be valid to the right of the center dashed curve.

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[16]For such a separation to occur it would be necessary for the particles to be present with different number density in different regions of the uniform background charge leading to a large charge unbalance between the regions occupied by the two phases. In a real system the background charge density would not be rigid and could adjust itself to keep the system nearly neutral in the regions occupied by the two phases at some cost in energy. Thus the thermodynamic properties of the background charge would be decisive in the determination of the actual region of coexistence of the two phases, but it would be a region and not a line in the (r_s, τ) plane. It should be added, however, that if we retain the assumption of a rigid background charge we have tacitly assumed that a finite droplet or superlattice structure with some spatial regions occupied by bcc and others by fcc lattice is not more stable in a transition region. The failure of this assumption could also lead to the possibility of a region of coexistence even in the presence of a rigid background charge.

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Electronic Hall Mobility in the Alkaline-Earth Fluorides†

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The electronic Hall mobility has been measured in additively colored samples of CaF_2, SrF_2, and BaF_2 over the temperature range 160–400 °K by a modified Redfield technique. In all cases the data show a temperature dependence which is much steeper than that predicted by the Feynman-Hellworth-Iddings-Platzman continuum polaron theory. It is suggested that a treatment of polaron transport which specifically considers the discreteness of the lattice may be necessary to fully understand transport in these intermediate-coupling materials.

I. INTRODUCTION

The alkaline-earth fluorides CaF_2, SrF_2, and BaF_2 have been of recent interest because of the photochromic behavior they exhibit when doped with rare-earth ions.[1,2] In addition, the simplicity of the fluorite structure has encouraged considerable theoretical work on their lattice dynamics[3,4] and dielectric properties.[5] The extensive body of measurements of the dielectric[6] and infrared optical properties[7,8] of these compounds permits reliable estimates to be made of many of the parameters crucial to any discussion of their electronic transport properties. The fact that all three fluorides can be made photoconducting by additive coloration[9,10] suggests that drift mobility and photo-Hall measurements might be utilized in an investigation of these transport properties. We present here a study of the temperature dependence of the electronic Hall mobility in all three alkaline-earth fluorides via a modified Redfield technique.

It is well known[11] that Hall-effect measurements have several advantages over other techniques in the study of the electronic properties of insulators. The first is that they are independent of shallow trapping effects; these effects often obscure the temperature dependence of the microscopic mobility in drift-mobility studies. The second is the availability of Hall techniques[12–14] which do not require the establishment of Ohmic contacts on wide-band-gap insulators, such as the alkaline-earth fluorides.

A glance at the similarity between the dielectric properties of the fluorides and those of the alkali halides[11] suggests that a discussion of their electronic-transport properties must proceed within the framework of polaron theory. In fact, the Fröhlich coupling constant, which describes the strength of the electron-phonon interaction in the continuum approximation, lies between 5 and 6 in the fluorides when the crystal band mass is equated to the free-electron value; these coupling constants are quite close to those computed for typical alkali halides.[11] It would, therefore, appear useful at this point to briefly review the polaron theories which have been applied to these materials with emphasis on their relevancy to experimental results on electronic-