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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1 REPORT NUMBER RDA-TR-124200-001	2 GOVT ACCESSION NO	3 RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) DEVELOPING NEW MATERIALS AT ELEVATED TEMPERATURES AND PRESSURES		5. TYPE OF REPORT & PERIOD COVERED Final, Sept. 1983 to February 1984
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Lester DeRaad Murray Gell-Mann Richard Latter		8. CONTRACT OR GRANT NUMBER(s) N00014-82-C-0749
9. PERFORMING ORGANIZATION NAME AND ADDRESS R & D Associates P.O. Box 9695 Marina del Rey, CA 90295		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Defense Advance Research Projects Agency 1400 Wilson Boulevard Arlington, VA 22209		12. REPORT DATE April 1984
		13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this report)

Approved for Public Release; Distribution Unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in block 20, if different from report)

DTIC
SELECTED
MAY 2 1 1984

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18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Metastable phases, crystal energy, band energy, KKR method,
structure constants

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The simple application of pressure and temperature is known to
cause phase (structural) changes in crystals. The changes will
not generally occur if the phases are relatively metastable, as
in the case of graphite and diamond. Special techniques are
required to induce these changes. Thus, it is quite possible
that phases exist that have gone undetected experimentally.
To find such metastable phases will require in general a priori
knowledge of their existence, that is, at least a crude (continued)

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Block 20. Abstract (Continued)

theoretical prediction of phase diagrams as a function of pressure and temperature. Limited progress toward this goal is described. The basic approach uses a crystal model closely related to the KKR method and an atomic potential described by the Thomas-Fermi statistical atom. Only the ion-ion interaction energy and the band energy are treated based on the conjecture that they are most sensitive to crystal structure. Within the KKR method for determining band energy, a new approach to the calculation of the structure constants is proposed and discussed.

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I. INTRODUCTION

The need for new materials with unique or improved properties or as substitutes for critical materials that are not native to the United States is a continuing and critical problem for the Department of Defense, for U.S. industry and for the U.S. political posture in general. The variety of techniques for finding such materials has been slowly growing--ranging from exploiting nature's creativity to employing a nuclear explosion to produce transuranic elements unknown in nature.

One technique of growing interest is rapid solidification and the production thereby of metallic glasses. By this means a number of potentially important new materials are being fabricated that could have extensive future industrial uses. However, the importance of developing new materials is so great that no avenue should go unexplored.

In this regard, there is one technique that has been almost entirely neglected, despite the fact that it has been extremely successful in producing valuable new materials in the few cases where it has been applied--this technique involves the employment of elevated temperature and pressure. By this means both diamond and cubic boron nitride have been synthesized and, in fact, are the only materials so formed that are in major commercial production. What is significant about these materials* is that neither is thermodynamically stable under ambient atmospheric conditions--although the transition probability to the normally stable state is so

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*Other materials that have been produced by this technique are principally minerals that have been synthesized for geo-physical research objectives, some simple inorganic compounds whose properties were not measured, and a few organic compounds.

small as to be entirely negligible. Thus, with the application of elevated temperature and pressure it is possible to create important industrial materials that cannot be created (in significant quantity) under normal atmospheric conditions and yet are metastable under these latter conditions.

What seems to be completely lacking is a _systematic_ effort to exploit the temperature/pressure technique--both experimentally and theoretically--for the production of new metastable materials for defense and industrial applications.

The intention of the work reported here is to assist in developing a methodology for creating such materials. A wide range of materials are known to undergo transformations to new phases with new properties upon application of pressure. However, these new phases change back to the original state when pressure returns to ambient.

Therefore, the basic problem that must be solved in order to fabricate useful materials at elevated pressure is to develop techniques to preserve the material after pressure is released. The solution of this problem is related intimately to the issue of how to form suitable new metastable materials in the first place. The reason is that if a new state is formed through a succession of equilibrium states by applying pressure, then the process is reversible (except possibly for minor time effects). Thus, either the formation or return to ambient conditions, or both, must involve nonequilibrium states.

In the rapid solidification process, sudden cooling inhibits the orderly transition through a succession of equilibrium states. Thus the final state (e.g. a metallic glass) is in

fact metastable with a negligible probability of transition
to the stable crystalline state. Accordingly with rapid
solidification, it is the return to ambient temperatures
that involves nonequilibrium states.

The direct analog of rapid solidification in the case of ele-
vated pressure is to form a new material at an elevated pres-
sure and then by sudden release of this pressure to attempt
to maintain the new material under ambient conditions albeit
in a metastable state. Since the rate of some mechanisms
that induce transitions decreases with decreasing pressure,
it is possible that the pressure analog of rapid solidifica-
tion will result in new materials. Even though this approach
looks promising, it has a disadvantage. Sudden changes of
pressure can be deleterious to high-pressure equipment. Thus,
unless special precautions are taken in the original equipment
design, this approach does not appear attractive. Since most
high-pressure equipment was not designed with this type of
operation in mind, this approach should probably not receive
primary emphasis--though it should be explored to an extent
consistent with safe operation of available high-pressure
presses, or equipment specially designed for safe rapid
decompression should be developed.

The primary experimental approach[*] should be analogous to
that employed in diamond synthesis. This approach is based
on the observation that since the new material to be synthe-
sized must be metastable under ambient atmospheric conditions,
the initial phase of the material will, in general, be meta-
stable in the high-pressure/temperature domain where the new
material is stable. For example, graphite is the stable form

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[*]Other approaches have been successfully employed in specific
cases but these do not have general applicability.

of carbon for pressures less than about 20 kbars, yet at 1 bar the rate of transition of diamond to graphite is so slow as to be entirely negligible. In fact, only by heating diamonds to about $800^{\circ}C$ at one atmosphere pressure does the transition become observable. Reciprocally, one can antici- pate (as has also been verified experimentally) that graphite will not make a transition to diamond simply by applying pressure in excess of 20 kbars, that is, simply by entering the diamond-stable region of the carbon-phase diagram. What is required to make the transition is some method for destroy- ing the graphite structure and allowing the carbon to reform as diamond, such as dissolution and reprecipitation or some form of excitation such as heating--perhaps even melting and resolidification. Both of the latter techniques have been used in synthesizing diamond from graphite.

More generally however, both techniques will be necessary to explore fully the phase diagram of materials at elevated pressure. If the new phase is contiguous to the liquidus domain, heating perhaps to melting followed by cooling and resolidification can be employed. If the new phase is not contiguous to the liquidus, then dissolution and reprecipi- tation will probably be necessary.

In summary, the basic experimental approach should involve the application of increasing pressure and, at each pressure, either the melting and resolidification of the specific mate- rial being studied or finding a solvent for the material and dissolving and reprecipitating the material.

Initially, it is the choice of materials for experimental investigation that presents the key uncertainty in exploring for new metastable phases. One must be able to define the

region of temperature and pressure where a particular phase is stable. Experimentally if one enters this region through a succession of equilibrum states, the entering phase will in general transform to the particular stable phase. On the other hand, if the entering phase is metastable relative to the stable phase no transition will take place. Experimentally, therefore one would have no indication that one had entered a region in which another phase was stable and therefore that it was worthwhile attempting to convert to this new phase. Only with a priori knowledge of the phase diagram could one be aware of the new phase. To obtain this knowledge, the new phase must exist because nature produced it, as was the case with diamond, or it must be inferred by other means, such as in the case of cubic boron nitride, or more generally one must be able to predict theoretically the phase diagrams of materials. The research described here was an attempt to develop a theoretical approach for guiding material choices (as well as exploiting such past experimental data as may be available). Since the approach was primarily to provide guidance for experiments rather than to improve predictive accuracy, emphasis was placed on developing simple, rapid and inexpensive computational techniques. The present report describes a partial step in this direction.

Since the primary objective is an approximate prediction of phase boundaries, the underlying emphasis was placed on comparing crystal structures for stability rather than obtaining an accurate description of a given structure. Accordingly, those aspects of a crystal that are insensitive to structural changes may be neglected or only crudely estimated.

The results so far obtained apply to zero temperature. It was not possible within the scope of the present effort to

include effects of temperature. With this limitation, the stable crystal structure is that one with minimum total energy at a given pressure or density. The total energy[1] of a crystal is generally expressed as a sum of the ion-ion interaction energy, the electron band energy, the Coulomb interaction energy of the band electrons, and the band electron exchange/correlation energy. The zero-point vibrational energy of the crystal and the interaction of the crystal zero-point vibration with the electrons is usually ignored, as is done here.

As a first step in an approximate theory, only the ion-ion interaction energy and the band energy have been treated since intuitively the remaining terms which depend only on the electron density distribution appear less sensitive in general to crystal structure. Furthermore, these other terms could add substantially to the computational expense. Only if this intuitive judgment does not lead to an approximate theory sufficient for guiding experiment will it be necessary to develop approximations for the other terms.

The ion-ion interaction energy is well-understood and is summarized in Section II. In Section III, the band energy is treated using the so-called "muffin-tin" potential. This potential consists of a spherically symmetric potential inside spheres centered on the ion sites and a constant potential outside the spheres. Using the fact that the potential outside the spheres is a constant and can be set equal to zero, a secular determinant for calculating the energy eigenvalues is derived in terms of the electron wave function and its derivative on the surface of the spheres. The result that we have obtained has turned out not to be new but to be closely related to that of Korringa[2] and equivalent

to that of Kohn and Rostoker,[3] and has been referred to for
sometime as the KKR method. To carry out the KKR method it
has been customary to start with a potential, like the Hartree-
Fock, solve the band problem, recalculate the potential,
spherically average it inside the spheres, and calculate a
new average outside the spheres, re-solve the band problem,
and iterate until self consistency is achieved. In contrast
we propose to use a simple model potential which if suffi-
ciently accurate to yield reasonable total band energies will
avoid the lengthy and costly iteration. The model potential
which we have chosen is that of the finite sized Thomas-Fermi
(TF) atom inside the spheres and constant outside. Using the
TF potential is particularly convenient since codes are avail-
able for calculating the surface values of the wave function
and its derivative as functions of atomic number, radius of
sphere, energy and angular momentum quantum number. In addi-
tion, comparison of energy eigenvalues using the TF atom and
those derived for Hartree-Fock indicates comparable agreement
with experiment.[4]

In the KKR method the most difficult quantities to calculate
are the so-called structure constants. The traditional method
to calculate these is based on a technique due to Ewald[5] and
is the most time consuming part of the band energy calcula-
tion. Consequently, we have investigated an alternate tech-
nique that might alleviate this difficulty. The details of
the technique are described in Section III. A suggestion for
possible further improvements is considered in Section V.

A computer program that reflects the current theoretical model
has been developed. The program for calculating the ion-ion
interaction energy is discussed in Section II and for the
band energy in Section IV.

In Section VI, we summarize what remains to be done to
finalize the initial theoretical model. We also discuss
what would be needed to validate the proposed approximate
model or to indicate that a more complex model is required.

II. ION-ION INTERACTION

The ion-ion energy per unit cell, E'_{cc}, is defined as the interaction energy of all the ions, treated as point charges, in the presence of a uniform background of negative charge density ρ_O,

$$\rho_O = - \frac{e}{\Omega} \sum_\alpha z_\alpha. \tag{1}$$

The total charge density is then

$$\rho(\vec{r}) = \sum_{N,\alpha} e \, z_\alpha \, \delta(\vec{r} - \vec{R}_N - \vec{a}_\alpha) + \rho_O \tag{2}$$

and the interaction energy is (in CGS units)

$$E = \frac{1}{2} \lim_{\lambda \to 0} \int d\vec{r} d\vec{r}\,' \, \frac{\rho(\vec{r})\rho(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} \, e^{-\lambda|\vec{r}-\vec{r}\,'|}, \tag{3}$$

where the self energy of the individual ions is understood to be excluded and λ is introduced to control the Coulomb singularity. We easily find

$$E'_{cc} = \frac{E}{N_T} = \frac{1}{2} e^2 \lim_{\lambda \to 0} {\sum_{\alpha\beta N}}' \, z_\alpha z_\beta \, \frac{e^{-\lambda|\vec{R}_N + \vec{a}_\alpha - \vec{a}_\beta|}}{|\vec{R}_N + \vec{a}_\alpha - \vec{a}_\beta|}$$

$$- \frac{2\pi e^2}{\Omega \lambda^2} \left(\sum_\alpha z_\alpha \right)^2, \tag{4}$$

where the prime on the sum indicates the $N = 0$, $\alpha = \beta$ terms are to be omitted.

It is convenient to remove the prime by considering the combination

$$E'_{cc} = \frac{1}{2} e^2 \lim_{\lambda \to 0} \lim_{r \to 0} \sum_{\alpha\beta} z_\alpha z_\beta \left[\sum_N \frac{e^{-\lambda|\vec{r} + \vec{a}_\beta - \vec{a}_\alpha - \vec{R}_N|}}{|\vec{r} + \vec{a}_\beta - \vec{a}_\alpha - \vec{R}_N|} \right.$$

$$\left. - \frac{e^{-\lambda r}}{r} \delta_{\alpha\beta} \right] - \frac{2\pi e^2}{\Omega \lambda^2} \left(\sum_\alpha z_\alpha \right)^2 , \qquad (5)$$

which can be rewritten using an identity due to Ewald,[5]

$$E'_{cc} = \frac{1}{2} e^2 \lim_{\lambda \to 0} \lim_{r \to 0} \sum_{\alpha\beta} z_\alpha z_\beta \left\{ - \frac{e^{-\lambda r}}{r} \delta_{\alpha\beta} \right.$$

$$+ \frac{4\pi}{\Omega} \sum_{\vec{G}} \frac{1}{G^2 + \lambda^2} e^{i \vec{G} \cdot (\vec{r} + \vec{a}_\beta - \vec{a}_\alpha)} e^{-(G^2 + \lambda^2)/\eta}$$

$$+ \frac{2}{\sqrt{\pi}} \sum_N \int_{\frac{1}{2}\sqrt{\eta}}^{\infty} d\zeta \, \exp\left[-(\vec{R}_N - \vec{r} - \vec{a}_\beta + \vec{a}_\alpha)^2 \zeta^2 - \lambda^2/4\zeta^2 \right] \left. \right\}$$

$$- \frac{2\pi e^2}{\Omega \lambda^2} \left(\sum_\alpha z_\alpha \right)^2 , \qquad (6)$$

where η is an arbitrary parameter greater than zero. The sensitive terms here are the $\vec{G} = 0$ term in the momentum space sum and the $N = 0$, $\alpha = \beta$ terms in the coordinate space sum. However, the limits of these terms are trivial leading to the result[6]

$$E_{cc}' = \frac{1}{2} e^2 \left\{ \frac{4\pi}{\Omega} \sum_{\alpha\beta} z_\alpha z_\beta \sum_{\vec{G}}' \frac{1}{G^2} \cos \vec{G} \cdot (\vec{a}_\alpha - \vec{a}_\beta) e^{-G^2/\eta} \right.$$

$$+ \sum_{\alpha\beta N}' z_\alpha z_\beta \frac{1}{|\vec{R}_N + \vec{a}_\alpha - \vec{a}_\beta|} \operatorname{erfc}\left(\frac{1}{2} \sqrt{\eta} \, |\vec{R}_N + \vec{a}_\alpha - \vec{a}_\beta| \right)$$

$$\left. - \frac{\sqrt{\eta}}{\sqrt{\pi}} \sum_\alpha z_\alpha^2 - \frac{4\pi}{\Omega} \frac{1}{\eta} \left(\sum_\alpha z_\alpha \right)^2 \right\}, \qquad (7)$$

where again the primes mean the $\vec{G} = 0$ term and the $N = 0$, $\alpha = \beta$ terms are excluded.

We have developed a computer code that calculates E_{cc}'. It assumes all quantities are in CGS and requires an input value for η. There is a library routine that calculates the complementary error function, erfc(x). Our experience has been that values of η on the order of 10^{16} cm^{-2} are reasonable and that the calculation is rapid, independent of the exact value of η.

III. BAND ENERGY

The present method of calculating the band energy is based on the "muffin-tin" approximation in which each atom of the crystal is contained within a sphere and the potential is assumed constant outside the spheres. The underlying concept for the method is to determine the wave functions for the valence and conduction electrons by expanding these wave functions as a superposition of atomic states within the spheres and then to match the resultant to a superposition of eigenstates external to the spheres where the potential is constant. This matching is done with the aid of Green's theorem relating the solution external to the spheres to the boundary values on the spheres.

This method, while conceptually different, leads to identical results to those of Korringa,[2] which is based on scattering theory. An equivalent Green's function approach was developed by Kohn and Rostoker[3] and Ham and Segall.[5]

To describe the method explicitly, we assume a general crystal with direct lattice vectors $\{\vec{R}_N\}$, reciprocal lattice vectors $\{\vec{G}\}$ and atomic locations within the unit cell $\{\vec{a}_\alpha\}$. Around each atomic location, a sphere of radius ρ_α is circumscribed in such a manner that the spheres do not overlap. Within each sphere the electronic wave function satisfies

$$H^\alpha \ \psi_\alpha(\vec{\rho}) \ = \ E \ \psi_\alpha(\vec{\rho}), \qquad (8)$$

where H^α is the Hamiltonian of the αth atom and E is the electron energy. Throughout this Section, we employ natural units where distances are in units of Bohr radii and energies are in Rybergs. The quantity k_0 is defined as

$$k_o = \sqrt{|E|} . \qquad (9)$$

The wave function, $\psi_\alpha(\vec{\rho})$, can be expressed as an expansion in spherical harmonics,

$$\psi_\alpha(\vec{\rho}) = \sum_{\ell,m} \left\{ \begin{matrix} i^\ell, & E>0 \\ 1, & E<0 \end{matrix} \right\} A^\alpha_{\ell m} R^\alpha_\ell(\rho) Y_{\ell m}(\hat{\rho}), \qquad (10)$$

where

$$H^\alpha_\ell R^\alpha_\ell(\rho) = E R^\alpha_\ell(\rho) \qquad (11)$$

and for positive energies the factor i^ℓ is introduced for later convenience. The wave function in Eq. (10) can be considered to be associated with the atom in the $\vec{R}_o = 0$ cell; wave functions in other cells have an additional factor $e^{i\vec{k}\cdot\vec{R}_N}$, where $\vec{k}$ is the electronic wave number.

Outside the atomic spheres, where the potential is assumed to be constant, the electron wave function, $\psi_o(\vec{r})$, can be expressed in terms of interior wave functions by means of Green's theorem. Thus we have

$$\psi_o(\vec{r}) = \frac{1}{4\pi} \sum_{N,\alpha} \int ds^\alpha_N \left[e^{i\vec{k}\cdot\vec{R}_N} \psi_\alpha(\vec{\rho}_\alpha) \frac{\partial G(\vec{r},\vec{r}_{N\alpha})}{\partial \rho_\alpha} \right.$$

$$\left. - e^{i\vec{k}\cdot\vec{R}_N} \frac{\partial \psi_\alpha(\vec{\rho}_\alpha)}{\partial \rho_\alpha} G(\vec{r},\vec{r}_{N\alpha}) \right] . \qquad (12)$$

This can be written as

$$\psi_o(\vec{r}) = \frac{1}{4\pi} \sum_\alpha \int ds^\alpha \left[\psi_\alpha(\vec{\rho}_\alpha) \frac{\partial F^\alpha(\vec{r})}{\partial \rho_\alpha} - \frac{\partial \psi_\alpha(\vec{\rho}_\alpha)}{\partial \rho_\alpha} F^\alpha(\vec{r}) \right], \qquad (13)$$

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where

$$F^{\alpha}(\vec{r}) = \sum_{N} e^{i\vec{k}\cdot\vec{R}_N} G(\vec{r},\vec{r}_{N\alpha}), \tag{14}$$

$$\vec{r}_{N\alpha} = \vec{R}_N + \vec{a}_{\alpha} + \vec{\rho}_{\alpha}. \tag{15}$$

Green's function satisfies

$$(\nabla^2 + E) G(\vec{r},\vec{r}_{N\alpha}) = -4\pi\delta(\vec{r}-\vec{r}_{N\alpha}) \tag{16}$$

or

$$G(\vec{r},\vec{r}') = \begin{cases} \dfrac{\cos k_o|\vec{r}-\vec{r}'|}{|\vec{r}-\vec{r}'|} & , E > 0, \\[4mm] \dfrac{e^{-k_o|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|} & , \quad E < 0. \end{cases} \tag{17}$$

Use has also been made of the equation satisfied by $\psi_o(\vec{r})$,

$$(\nabla^2 + E) \psi_o(\vec{r}) = 0, \tag{18}$$

since the outside constant potential has been chosen as the reference zero for energies.

The complete wave function $\psi_{\vec{k}}(\vec{r})$ is thus determined by

$$\psi_{\vec{k}}(\vec{r}) = \psi_{\alpha}(\vec{\rho}) \quad \text{inside the } \alpha^{\text{th}} \text{ sphere, } N = 0,$$

$$= \psi_o(\vec{r}) \quad \text{outside the spheres.} \tag{19}$$

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However, $\psi_{\vec{k}}(\vec{r})$ involves the unknown constants $A^\alpha_{\ell m}$ and the energy E, both of which are functions of the electronic wave number $\vec{k}$. To determine these unknowns, one uses Eq. (13) and lets $\vec{r} \rightarrow \vec{a}_\beta + \vec{\rho}_\beta$. Thus the requirement

$$\psi_0(\vec{r}) \rightarrow \psi_\beta(\vec{\rho}_\beta) \tag{20}$$

implies

$$\psi_\beta(\vec{\rho}_\beta) = \frac{1}{4\pi} \sum_\alpha \int ds^\alpha \left[\psi_\alpha(\vec{\rho}_\alpha) \frac{\partial F^\alpha(\vec{\rho}_\beta + \vec{a}_\beta)}{\partial \rho_\alpha} - \frac{\partial \psi_\alpha(\vec{\rho}_\alpha)}{\partial \rho_\alpha} F^\alpha(\vec{\rho}_\beta + \vec{a}_\beta) \right]. \tag{21}$$

From Eq. (10), it is clear that Eq. (21) constitutes a set of linear equations in the unknowns $A^\alpha_{\ell m}$. For this set to have a nontrivial solution, the determinant of the coefficients of the $A^\alpha_{\ell m}$'s must vanish. Setting the determinant equal to zero results in a transcendental equation for E as a function of $\vec{k}$ (the so-called secular equation). The solution for E vs $\vec{k}$ defines the electronic band structure and, moreover, determines the values of the $A^\alpha_{\ell m}$'s when the requirement of wave function normalization is added. Once E vs $\vec{k}$ and the values of $A^\alpha_{\ell m}$ are determined, then Eq. (19) defines the overall system wave function for each $\vec{k}$-value. The E vs $\vec{k}$ results lead to the total band energy by summing to the Fermi energy. The wave functions allow a calculation of the electronic charge density which determines the Coulomb and correlation and exchange contributions to the total energy. The most critical element in carrying out the above procedure is the evaluation of $F^\alpha(\vec{\rho}_\beta + \vec{a}_\beta)$ defined by Eqs. (14) and (17). The reason is that these quantities are defined by infinite series that are rather slowly convergent and may in fact require several thousand terms to achieve adequate accuracy.

Thus computational efficiency and the choice of form for $F^{\alpha}(\vec{\rho}_{\beta}+\vec{a}_{\beta})$ become crucial. Most of the effort in exploiting the present method has focused on just these points.

The explicit form for $F^{\alpha}(\vec{r})$ will now be derived. We will consider the positive energy case but the corresponding equations for negative energy are either obvious or will be treated explicitly. From Eqs. (14) and (17), we have

$$F_{\alpha}(\vec{r}) = \sum_{N} e^{i\vec{k}\cdot\vec{R}_N} \frac{\cos k_0 |\vec{r}-\vec{r}_{N\alpha}|}{|\vec{r}-\vec{r}_{N\alpha}|}. \tag{22}$$

It is clear that within a given unit cell N, the only singularity of $F^{\alpha}(\vec{r})$ results from the single term

$$\frac{\cos k_0 |\vec{r}-\vec{r}_{N\alpha}|}{|\vec{r}-\vec{r}_{N\alpha}|},$$

which satisfies the inhomogeneous Eq. (16). The remaining infinite sum satisfies the homogeneous equation

$$(\nabla^2+E) \left\{ F_{\alpha}(\vec{r}) - e^{i\vec{k}\cdot\vec{R}_N} \frac{\cos k_0 |\vec{r}-\vec{r}_{N\alpha}|}{|\vec{r}-\vec{r}_{N\alpha}|} \right\} = 0. \tag{23}$$

Since the above two properties apply for all N, we can choose, for convenience, N = 0, for which

$$\vec{r}_{O\alpha} = \vec{a}_{\alpha} + \vec{\rho}_{\alpha}'. \tag{24}$$

We are interested in $F_{\alpha}(\vec{r})$ when [cf. Eq. (21)]

$$\vec{r} \rightarrow \vec{a}_{\beta} + \vec{\rho}_{\beta} \tag{25}$$

and this quantity can be considered to be a function of $\vec{\kappa}$,

$$\vec{R} = \vec{\rho}_\beta - \vec{\rho}_\alpha'. \qquad (26)$$

If we define the functions $H_\alpha(\vec{R})$ and $D_\alpha(\vec{R})$ as

$$F_\alpha(\vec{a}_\beta + \vec{\rho}_\beta) \equiv H_\alpha(\vec{R}) = \frac{\cos k_o R}{R} \delta_{\alpha\beta} + D_\alpha(\vec{R}), \qquad (27)$$

it is clear that for sufficiently small values of R, $D_\alpha(\vec{R})$ satisfies [cf. Eq. (23)]

$$(\nabla^2_{\vec{R}} + E) \ D_\alpha(\vec{R}) = 0. \qquad (28)$$

This will be true so long as R is not so large as to encounter any singularities except the possible one (for $\alpha = \beta$) at R = 0. It is sufficient to assume that

$$R < R_N, \ N \neq 0, \ \alpha = \beta,$$

$$R < |\vec{a}_\beta - \vec{a}_\alpha + \vec{R}_N|, \ \alpha \neq \beta. \qquad (29)$$

Since $D_\alpha(\vec{R})$ satisfies Eq. (28), it must have the general form

$$D_\alpha(\vec{R}) = 4\pi \sum_{L,M} i^L D^{\alpha\beta}_{LM} \ \text{FAC}(L,M) \begin{Bmatrix} j_L(k_o R), & E > 0 \\ \tilde{I}_L(k_o R), & E < 0 \end{Bmatrix} Y_{LM}(\hat{R}), \qquad (30)$$

where $Y_{LM}(\hat{R})$ are spherical harmonics, $D_{LM}^{\alpha\beta}$ are the structure constants and the factor

$$FAC(L,M) = \begin{cases} 1, M \geq 0 \\ (-1)^M, M < 0 \end{cases} \sqrt{\frac{2L+1}{4\pi} \frac{(L-|M|)!}{(L+|M|)!}} \qquad (31)$$

has been introduced for later convenience. For positive energies, $j_L(x)$ are the spherical Bessel functions while for negative energies, $\tilde{I}_L(x)$ are the modified spherical Bessel functions, defined as

$$\tilde{I}_L(x) = (-i)^L j_L(ix). \qquad (32)$$

Equation (30) combined with Eq. (27) gives the most general form for $H_\alpha(\vec{R})$ for sufficiently small R.

An alternate form for $H_\alpha(\vec{R})$ can be derived by a straight-forward Fourier series transformation of Eq. (22) multiplied by $e^{-i\vec{k}\cdot\vec{r}}$ since the combination is then periodic in the lattice vectors $\vec{R}_N$. We easily find

$$H_\alpha(\vec{R}) = \frac{4\pi}{\Omega} \sum_{\vec{G}} \frac{e^{i(\vec{k}+\vec{G})\cdot(\vec{a}_\beta - \vec{a}_\alpha)}}{(\vec{k}+\vec{G})^2 - E} e^{i(\vec{k}+\vec{G})\cdot\vec{R}}, \qquad (33)$$

which is correct for both positive and negative energies. By making use of the well-known relationship,

$$e^{i(\vec{k}+\vec{G})\cdot\vec{R}} = 4\pi \sum_{L,M} i^L j_L(|\vec{k}+\vec{G}|R) Y_{LM}^*(\widehat{\vec{k}+\vec{G}}) Y_{LM}(\hat{R}), \qquad (34)$$

we can derive an explicit expression for the structure constants, $D_{LM}^{\alpha\beta}$, contained in

$$D_{LM}^{\alpha\beta} \begin{Bmatrix} j_L \ (k_o R), \ E > 0 \\ \\ \tilde{I}_L \ (k_o R), \ E < 0 \end{Bmatrix} = \frac{4\pi}{\Omega} \sum_{\vec{G}} \frac{e^{i(\vec{k}+\vec{G})\cdot(\vec{a}_\beta - \vec{a}_\alpha)}}{(\vec{k}+\vec{G})^2 - E} \ j_L(|\vec{k}+\vec{G}|R) \frac{Y^*_{LM}(\widehat{\vec{k}+\vec{G}})}{FAC(L,M)}$$

$$- \frac{1}{R} \ \delta_{L0} \ \delta_{M0} \ \delta_{\alpha\beta} \begin{Bmatrix} \cos k_o R, \ E > 0 \\ \\ e^{-k_o R}, \quad E < 0 \end{Bmatrix}. \tag{35}$$

Once we have introduced the structure constants, we can derive a convenient expression for $H_\alpha(\vec{R})$ that separates the angular dependences of $\hat{\rho}_\beta$ and $\hat{\rho}'_\alpha$. This derivation employs the following well-known results [recall Eq. (26)]:

$$i^L \ j_L \ (k_o R) \ Y_{LM} \ (\hat{R})$$

$$= 4\pi \sum_{\ell m} \ \sum_{\ell' m'} \ i^{\ell - \ell'} j_\ell (k_o \rho_\beta) j_{\ell'}(k_o \rho'_\alpha) C^{LM}_{\ell m, \ell' m'} Y_{\ell m}(\hat{\rho}_\beta) Y^*_{\ell' m'}(\hat{\rho}'_\alpha), \tag{36}$$

$$\tilde{I}_L \ (k_o R) \ Y_{LM} \ (\hat{R})$$

$$= 4\pi \sum_{\ell m} \ \sum_{\ell' m'} (-1)^{\ell'} \tilde{I}_\ell (k_o \rho_\beta) \tilde{I}_{\ell'}(k_o \rho'_\alpha) C^{LM}_{\ell m, \ell' m'} Y_{\ell m}(\hat{\rho}_\beta) Y^*_{\ell' m'}(\hat{\rho}'_\alpha), \tag{37}$$

$$\frac{\cos k_o R}{R} = -4\pi \ k_o \ \sum_{LM} j_L(k_o \rho'_\alpha) n_L(k_o \rho_\beta) Y_{LM}(\hat{\rho}_\beta) Y^*_{LM}(\hat{\rho}'_\alpha), \tag{38}$$

$$\frac{e^{-k_o R}}{R} = 4\pi \ k_o \ \frac{2}{\pi} \ \sum_{LM} \tilde{I}_L(k_o \rho'_\alpha) \tilde{K}_L(k_o \rho_\beta) Y_{LM}(\hat{\rho}_\beta) Y^*_{LM}(\hat{\rho}'_\alpha). \tag{39}$$

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In Eqs. (36) and (37), the quantity $C_{\ell m, \ell'm'}^{LM}$ is[7]

$$C_{\ell m, \ell'm'}^{LM} = \int d\hat{\Omega} \, Y_{LM}^*(\hat{\Omega}) \, Y_{\ell m}^*(\hat{\Omega}) \, Y_{\ell'm'}(\hat{\Omega})$$

$$= \left[\frac{(2L+1)(2\ell+1)}{4\pi(2\ell'+1)} \right]^{1/2} C(L,\ell,\ell';M,m) C(L,\ell,\ell';0,0), \qquad (40)$$

where $C(L,\ell,\ell';M,m)$ are Clebsch-Gordan coefficients. In Eqs. (38) and (39), we have assumed

$$\rho_\beta > \rho_\alpha', \qquad (41)$$

which is the case of interest and $\tilde{K}_L(x)$ are again certain modified spherical Bessel functions defined as

$$\tilde{K}_L(x) = \frac{\pi}{2} i^{L+2} h_L^{(1)}(ix). \qquad (42)$$

Making use of the above relationships in the expression for $\vec{H}_\alpha(\vec{R})$, we find

$$H_\alpha(\vec{\rho}_\beta - \vec{\rho}_\alpha') = 4\pi \sum_{\ell m} \sum_{\ell'm'} \left[4\pi \sum_{LM} D_{LM}^{\alpha\beta} C_{\ell m, \ell'm'}^{LM} FAC(L,M) \right] Y_{\ell m}(\hat{\rho}_\beta) Y_{\ell'm'}^*(\hat{\rho}_\alpha')$$

$$\times \left\{ \begin{array}{l} i^{\ell-\ell'} j_\ell(k_o\rho_\beta) j_\ell(k_o\rho_\alpha'), \ E > 0 \\[2ex] (-1)^{\ell'} \tilde{I}_\ell(k_o\rho_\beta) \tilde{I}_{\ell'}(k_o\rho_\alpha'), \ E < 0 \end{array} \right\}$$

$$-4\pi k_o \, \delta_{\alpha\beta} \sum_{LM} Y_{LM}(\hat{\rho}_\beta) Y_{LM}^*(\hat{\rho}_\alpha') \left\{ \begin{array}{l} j_L(k_o\rho_\alpha') n_L(k_o\rho_\beta), \ E > 0 \\[2ex] -\frac{2}{\pi} \tilde{I}_L(k_o\rho_\alpha') \tilde{K}_L(k_o\rho_\beta), \ E < 0 \end{array} \right\}.$$

$$(43)$$

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If Eqs. (43) and (10) are now substituted into Eq. (21), one obtains a system of linear homogeneous equations for the determination of the coefficients $A_{\ell'm'}^{\alpha}$. Namely, we have

$$\sum_{\alpha\ell'm'} A_{\ell'm'}^{\alpha} \; Q_{\ell'm'\ell m}^{\alpha\beta} = 0,\tag{44}$$

where the matrix Q is

$$Q_{\ell'm'\ell m}^{\alpha\beta} = \left[\sum_L \begin{Bmatrix} 1, & E>0 \\ i^L, & E<0 \end{Bmatrix} D_{LM}^{\alpha\beta} \; \text{FAC (L,M)} \; C_{\ell m,\ell'm'}^{LM} \; V_{\ell'}^{\alpha} \right.$$

$$\left. + \; \delta_{\ell\ell'} \; \delta_{mm'} \; \delta_{\alpha\beta} \; U_{\ell}^{\alpha} \right] \begin{Bmatrix} j_{\ell}(k_o\rho_\beta), & E > 0 \\ \tilde{I}_{\ell}(k_o\rho_\beta), & E < 0 \end{Bmatrix}.\tag{45}$$

The quantities V_{ℓ}^{α} and U_{ℓ}^{α} are

$$V_{\ell}^{\alpha} = 4\pi\rho_\alpha^2 \begin{Bmatrix} k_o \; j_{\ell}'(k_o\rho_\alpha) R_{\ell}^{\alpha} - j_{\ell}(k_o\rho_\alpha)(R_{\ell}^{\alpha})' \; , & E > 0 \\ (-1)^{\ell} \left[k_o\tilde{I}_{\ell}'(k_o\rho_\alpha) R_{\ell}^{\alpha} - \tilde{I}_{\ell}(k_o\rho_\alpha)(R_{\ell}^{\alpha})' \right], & E < 0 \end{Bmatrix},\tag{46}$$

$$U_{\ell}^{\alpha} = \rho_\alpha^2 \; k_o \begin{Bmatrix} -k_o n_{\ell}'(k_o\rho_\alpha) R_{\ell}^{\alpha} + n_{\ell}(k_o\rho_\alpha)(R_{\ell}^{\alpha})' \; , & E > 0 \\ k_o\frac{2}{\pi}\tilde{K}_{\ell}'(k_o\rho_\alpha) R_{\ell}^{\alpha} - \frac{2}{\pi}\tilde{K}_{\ell}(k_o\rho_\alpha)(R_{\ell}^{\alpha})' , & E < 0 \end{Bmatrix}.\tag{47}$$

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Here, R_{ℓ}^{α} and $(R_{\ell}^{\alpha})'$ are the wave function and its derivative, respectively, evaluated at $\rho = \rho_{\alpha}$. In order to express Q in the form of Eq. (45), it is necessary to use the Wronskian of the (modified) spherical Bessel functions,

$$W\left\{j_{\ell}(x), \, n_{\ell}(x)\right\} = \frac{1}{x^2},$$

$$W\left\{\tilde{I}_{\ell}(x), \, \tilde{K}_{\ell}(x)\right\} = -\frac{\pi}{2}\frac{1}{x^2}. \tag{48}$$

In order for the system of equations, Eq. (44), to have a solution,

$$\det\left|Q^{\alpha\beta}_{\ell'm'\ell m}\right| = 0. \tag{49}$$

This secular equation determines E as a function of $\vec{k}$ and thereby defines the band structure.

For each E that satisfies Eq. (49), one can determine the solutions $A_{\ell m}^{\alpha}$ of Eq. (44) up to a common unknown factor. This latter is determined by the requirement that the wave function Eq. (19) be normalized. After normalization, Eq. (10) specifies the interior wave function and Eq. (12), the exterior. With the band structure and crystalline wave function specified, the total crystal energy can be found. With our present initial model, normalization of the wave function is not necessary.

Experience indicates that the determination of the band energy requires the solution of Eq. (49) for E at several thousand values of $\vec{k}$. However, because of the complex transcendental character of the determinant, it must be evaluated

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at sufficient E values to permit interpolation for that value of E that satisfies Eq. (49) for a given $\vec{k}$ vector. Since the determinant involves all the $D_{LM}^{\alpha\beta}$'s, which depend both on E and $\vec{k}$, it is clear that the $D_{LM}^{\alpha\beta}$'s will have to be evaluated at many tens of thousands of $\vec{k}$ values. As a consequence the time to calculate the infinite series $D_{LM}^{\alpha\beta}$ can dominate the time, and therefore the cost, of the overall calculation. Thus minimizing this time is vital.

Up to now, the literature has emphasized only one approach to improving the rate of convergence of the $D_{LM}^{\alpha\beta}$'s, namely the application of the Ewald method. While substantial improvement is possible this way, it suffers from the requirement that for a given accuracy either time-consuming incomplete gamma functions must be evaluated or a large number of terms in the infinite series must be calculated.

In the present work, what appears to be an entirely new approach is being explored. The basis of this approach rests on the observation that $D_{LM}^{\alpha\beta}$ as given in Eq. (35) is independent of R subject only to the constraint Eq. (29).

Thus we can multiply Eq. (35) by an arbitrary function f(R) and integrate on R up to some upper limit constrained by Eq. (29). Thus, $D_{LM}^{\alpha\beta}$ can be rewritten as

$$D_{LM}^{\alpha\beta} = \frac{4\pi}{\Omega}\, \frac{1}{H_L} \sum_{\vec{G}} \frac{e^{i\,(\vec{k}+\vec{G})\cdot(\vec{a}_\beta-\vec{a}_\alpha)}}{(\vec{k}+\vec{G})^2 - E}\, \frac{Y_{LM}^{*}(\widehat{\vec{k}+\vec{G}})}{FAC(L,M)}\, F_L(|\vec{k}+\vec{G}|R)$$

$$- \delta_{L0}\, \delta_{M0}\, \delta_{\alpha\beta}\, k_o\, \frac{\bar{\bar{H}}}{H_0}\,, \tag{50}$$

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where we have defined the following functions:

$$F_L(x) = \int_0^1 dy \, f_L(y) \, j_L(xy), \tag{51}$$

$$H_L = \begin{cases} F_L(k_o R), & E > 0, \\ \int_0^1 dy \, \hat{f}_L(y) \, \tilde{I}_L(k_o Ry), & E < 0, \end{cases} \tag{52}$$

$$\bar{H} = \begin{cases} - \int_0^1 dy \, f_0(y) \, n_0(k_o Ry), & E > 0, \\ \frac{2}{\pi} \int_0^1 dy \, f_0(y) \, \tilde{K}_0(k_o Ry), & E < 0. \end{cases} \tag{53}$$

Since, for a given value of $\vec{k}$, Eq. (50) must be evaluated for many values of E, calculation time would be prohibitive even with improved convergence of the sum. This problem can be minimized by use of the identity

$$\frac{1}{|\vec{k}+\vec{G}|^2 - E} = \frac{1}{|\vec{k}+\vec{G}|^2} \sum_{m=0}^{N-1} \left(\frac{E}{|\vec{k}+\vec{G}|^2} \right)^m + \left(\frac{E}{|\vec{k}+\vec{G}|^2} \right)^N \frac{1}{|\vec{k}+\vec{G}|^2 - E} \tag{54}$$

which allows E to be factored from the sum except for the last term in Eq. (54). However, even for modest values of N, the last term can be made to converge extremely fast. The actual implementation of Eq. (54) will be discussed below in connection with the computer program for calculating $D_{LM}^{\alpha\beta}$.

We now turn to the choice of $f(y)$. We require first that $f(y)$ be such that the integrals over y be analytically evaluable.

If numerical integration were required, the time for evaluation would be prohibitive. A second desirable property of $f(y)$ is that it vanish at $y = 0$ and $y = 1$. This property implies that

$$\int_0^1 dy\ f(y)\ j_L(|\vec{k}+\vec{G}|Ry) \sim \frac{1}{|\vec{k}+\vec{G}|^n} \qquad (55)$$

for large $|\vec{k}+\vec{G}|$, where n depends upon the order of the zero at $y = 0$ and $y = 1$.

Although a large number of functions satisfy these conditions, we have concentrated on the following two:

$$f_1(y) = \frac{1}{2^\mu}\frac{1}{\mu!}\ y^{L+2}\ (1-y^2)^\mu, \qquad (56)$$

$$f_2(y) = \frac{2}{L!}\ y^{L+1}\ (1-y^2)^L. \qquad (57)$$

For these functions, we find for $F_L(x)$, Eq. (51),

$$f = f_1\ :\quad F_L(x) = \frac{j_{L+\mu+1}(x)}{x^{\mu+1}}, \qquad (58)$$

$$f = f_2\ :\quad F_L(x) = \left[j_L\left(\frac{x}{2}\right)\right]^2 \Big/ \left(\frac{x}{2}\right)^L. \qquad (59)$$

The results for H_L and $\overline{H}$ will be discussed below. It is clear from Eqs. (58) and (59) that R should be chosen as

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large as possible consistent with Eq. (29). However, which
form provides the greater convergence improvement is more
subtle. To clarify, one observes that for small argument

$$j_n(x) \sim \frac{2\Gamma(n+1)}{\Gamma(2n+2)} x^n \qquad (60)$$

and for large arguments

$$j_n(x) \sim \frac{1}{x} \sin\left(x - \frac{n\pi}{2}\right). \qquad (61)$$

Eq. (60) points up the known result that the larger n becomes,
the larger x must be before Eq. (61) starts to apply. Thus,
in Eq. (58) the larger n becomes the more is the number of
$\vec{G}$ values required before the denominator can speed conver-
gence. On the other hand, in Eq. (59) the order of the
spherical Bessel function is small but the convergence factor
in the denominator is constrained.

Taking account of these conflicting advantages suggests that
Eq. (58) is probably to be preferred for low values of L and
modest values of μ, while Eq. (59) is to be preferred for
larger values of L.

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IV. COMPUTER PROGRAM DEVELOPMENT

In developing the computer program a number of assumptions have been made:

- the maximum ℓ of interest for the wave function is $\ell = 3$ and, therefore, the maximum L of interest for the structure constants is L = 6,

- the maximum number of ions per unit cell is 2, though this restriction may be readily removed,

- outward recurrence relations are acceptable to calculate $j_\ell(x)$ and $\widetilde{I}_\ell(x)$,

- $f_1(y)$ with $\mu = 5$ is used for L = 0 - 4 and $f_2(y)$ is used for L = 5 - 6,

- the parameter N in Eq. (54) is taken to be 10.

The last three of these assumptions will be discussed in Section VI.

Once the lattice has been specified (see Appendix), approximately 4000 $\vec{G}$ values are computed and sorted according to length. A shell structure in $\vec{G}$ space is defined to test for convergence of the expansion coefficients. At present, this shell structure is externally prescribed.

The first step is to calculate expansion coefficients based on Eq. (54). We define the two quantities BR and BI, for $M \geq 0$, by

$$\left.\begin{array}{c} BR(L,M,I) \\[2em] BI(L,M,I) \end{array}\right\} = \sum_{\vec{G}} \frac{P(L,M)}{\left[|\vec{G}+\vec{k}|^2\right]^I} \; F_L(R|\vec{G}+\vec{k}|) \left\{\begin{array}{c} \cos M\phi \\[1em] \sin(-M)\phi \end{array}\right\}, \qquad (62)$$

where $P(L,M)$ are the usual associated Legendre polynomials and ϕ is the azimuthal angle of the vector $\vec{G}+\vec{k}$. If there are two ions per unit cell, we also define the four quantities B1, B2, B3 and B4, for $M \geq 0$, as

$$\left.\begin{array}{c} B1(L,M,I) \\ B2(L,M,I) \\ B3(L,M,I) \\ B4(L,M,I) \end{array}\right\} = \sum_{\vec{G}} \frac{P(L,M)}{\left[|\vec{G}+\vec{k}|^2\right]^I} \; F_L(R|\vec{G}+\vec{k}|) \left\{\begin{array}{c} \cos M\phi \cos x \\ \sin(-M)\phi \cos x \\ \cos M\phi \sin x \\ \sin(-M\phi)\sin x \end{array}\right\}, \quad (63)$$

where

$$x = (\vec{a}_2 - \vec{a}_1) \cdot (\vec{G}+\vec{k}) . \qquad (64)$$

As each shell is calculated, the fractional change in the quantity

$$(BR)^2 + (BI)^2$$

is determined for those values of L, M and I considered in the shell. If for a given L, M and I, the change is less than some prescribed amount, that L, M and I is considered to have converged and will not be calculated for the next succeeding shell. Consequently, as we go through the shells, contributions are calculated for fewer and fewer expansion coefficients until all have converged. At present, no testing is done on B1-4.

The program for this part of the calculation has been optimized to a large extent but some improvement cannot be ruled out. Most of the testing of this portion of the program assumed a fcc lattice with a volume of $2\pi^3$, one ion per unit cell and a $\vec{k}$ of

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$$\vec{k} = (0.3, 0.4, 0.5). \tag{65}$$

The maximum value for the parameter R is then

$$R = 4.4. \tag{66}$$

The reason for these choices is that published values[8] for the structure constants at the energy

$$E = 0.656 \tag{67}$$

were available for comparison. We found that with these choices (particularly R), all the expansion coefficients converged to an accuracy of 10^{-3} with about 1000 $\vec{G}$ points. To improve the accuracy to 10^{-4} required about 2000 $\vec{G}$ points. If R is decreased to 2.7, some of the expansion coefficients did not converge to an accuracy of 10^{-3} even with 4000 $\vec{G}$ points. This point will be discussed in Section V.

Once the expansion coefficients for a given $\vec{k}$ value have been evaluated, the determinant for a predetermined set of energies can be calculated. To do so a set of coefficients CR(L, M), CI(L, M) and if appropriate, C1-4(L, M) are calculated. These are defined, as in Eqs. (62) and (63), respectively, by the substitution

$$\frac{1}{\left[\,|\vec{G}+\vec{k}|^2\,\right]^I} \;\rightarrow\; \frac{1}{\left[\,|\vec{G}+\vec{k}|^2\,\right]^{10}} \; \frac{1}{|\vec{G}+\vec{k}|^2 - E}. \tag{68}$$

The calculation is done for the first shell only and no test of convergence is necessary because of the rapidity of convergence. Based on Eq. (54), the appropriate combinations are

$$DX(L,M) = \frac{4\pi}{\Omega} \left\{ \sum_{I=1}^{10} E^{I-1} BX(L,M,I) + E^{10} CX(L,M) \right\}, \qquad (69)$$

where $X = R$, I, 1-4. Simple linear combinations of these quantities, divided by H_L, then yield $D_{LM}^{\alpha\beta}$, Eq. (50), except for the $\bar{H}$ term. We note that for $E < 0$, H_L is simply ($x = k_0 R$)

$$f = f_1 \quad : \quad H_L = \tilde{I}_{L+\mu+1}(x)/x^{\mu+1},$$

$$f = f_2 \quad : \quad H_L = \left[\tilde{I}_L \left(\frac{x}{2} \right) \right]^2 / \left(\frac{x}{2} \right)^L. \qquad (70)$$

For $L = 0$, with $f_1(y)$ given by Eq. (56) and $\mu = 5$, the calculation of $\bar{H}$, Eq. (53), is trivial.

The portion of the program for calculating the structure constants has been tested and improved using the standard lattice defined above. Typically, the structure constants have the same relative accuracy as the expansion coefficients. The only exceptions may be structure constants with abnormally small values. In Table 1, we present the structure constants as given in Ref. 8 and our calculation of them using error measures of 10^{-4} and 10^{-3}, respectively. Since the normalization in Ref. 8 is different from ours, Eq. (50), we have converted our normalization for ease of comparison. Notice that for $M \geq 0$ ($M < 0$), the structure function is related to BR (BI), Eq. (62).

Once the structure constants have been determined, the matrix elements readily follow. The quantities

TABLE 1. STRUCTURE CONSTANTS, fcc, VOLUME = $2\pi^3$

$\vec{k}$ = (0.3, 0.4, 0.5), E = 0.656

L	M	D_{LM}(Davis)	$D_{LM}(10^{-4})$	$D_{LM}(10^{-3})$
0	0	0.3637069	0.363707	0.363707
1	-1	0.4729255	0.472924	0.472922
1	0	0.5585931	0.558592	0.558583
1	1	0.3855073	0.385506	0.385504
2	-2	0.1383943	0.138390	0.138385
2	-1	0.3854948	0.385489	0.385477
2	0	0.2294027	0.229400	0.229400
2	1	0.2425004	0.242496	0.242488
2	2	-0.1231771	-0.123176	-0.123175
3	-3	0.3342447	0.334248	0.334245
3	-2	0.7787625	0.778762	0.778763
3	-1	0.3760202	0.376019	0.376012
3	0	-0.3433054	-0.343305	-0.343308
3	1	0.3140171	0.314016	0.314011
3	2	-0.0644856	-0.064484	-0.064482
3	3	-0.3585324	-0.358534	-0.358529
4	-4	-0.1350521	-0.135051	-0.135050
4	-3	-0.5645986	-0.564611	-0.564689
4	-2	0.0665038	0.066486	0.066451
4	-1	0.4518756	0.451877	0.451905
4	0	-0.2631646	-0.263159	-0.263139
4	1	0.4007033	0.400704	0.400723
4	2	-0.1747519	-0.174749	-0.174753
4	3	0.1291246	0.129140	0.129196
4	4	0.2032239	0.203229	0.203258
5	-5	0.4958597	0.495869	0.495955
5	-4	-0.0768520	-0.076852	-0.076854
5	-3	0.8811268	0.881139	0.881165

TABLE 1. STRUCTURE CONSTANTS, fcc, VOLUME = $2\pi^3$

$\vec{k}$ = (0.3, 0.4, 0.5), E = 0.656 (CONCLUDED)

L	M	$D_{LM}(Davis)$	$D_{LM}(10^{-4})$	$D_{LM}(10^{-3})$
5	-2	0.2049815	0.204982	0.204986
5	-1	-0.9030668	-0.903089	-0.903093
5	0	0.6678767	0.667894	0.668039
5	1	-0.6314083	-0.631422	-0.631417
5	2	-0.4744635	-0.474484	-0.474487
5	3	-0.8026519	-0.802659	-0.802677
5	4	-1.5614385	-1.56146	-1.56226
5	5	0.0352270	0.035233	0.035293
6	-6	4.3426328	4.34269	4.34528
6	-5	-2.2561097	-2.25614	-2.25619
6	-4	-0.3471268	-0.347127	-0.347125
6	-3	4.5963681	4.59643	4.59700
6	-2	-2.3159161	-2.31596	-2.31813
6	-1	3.5271685	3.52722	3.52776
6	0	-1.1349680	-1.13498	-1.13508
6	1	3.0624581	3.06251	3.06295
6	2	0.1585912	0.158593	0.158807
6	3	-4.1491049	-4.14916	-4.14964
6	4	0.9372909	0.937309	0.937489
6	5	-1.4263739	-1.42640	-1.42644
6	6	0.3302557	0.330258	0.330567

$$CB(\ell m, \ell'm', L) = FAC(L,M) \; C^{LM}_{\ell m, \ell'm'} \tag{71}$$

are calculated early in the program and stored for use as necessary. For a prescribed set of energies, the quantities V^{α}_{ℓ}, Eq. (46), and U^{α}_{ℓ}, Eq. (47), are also calculated and stored. The matrix elements Q, Eq. (45), are computed and the determinant calculated. This final process has been programmed but not checked extensively.

Finally, a word about V^{α}_{ℓ} and U^{α}_{ℓ} is required. An existing Thomas-Fermi program provides the basic information ιor the wave function and its derivative, namely E(TF), PSI(ℓ,α) and DPSI/DR(ℓ,α) which are related to the above quantities by

$$E = -E(TF),$$

$$R^{\alpha}_{\ell} = PSI(\ell,\alpha),$$

$$(R^{\alpha}_{\ell})' = DPSI/DR(\ell,\alpha) - \frac{1}{\rho_{\alpha}} PSI(\ell,\alpha). \tag{72}$$

The calculation of V^{α}_{ℓ} and U^{α}_{ℓ} using the provided quantities has been programmed but not checked.

The complete program was run using carbon wave functions with $\rho_{\alpha} = 1.26$ and a set of energies from -4 to $+2$ at intervals of 0.1. A simple cubic lattice was assumed with a volume of 19.2 and the value of R was taken to be 2.5, near its maximum value for this lattice. The $\vec{k}$ vector was chosen to be

$$\vec{k} = (0.1, 0.2, 0.3). \tag{73}$$

The determinant as a function of energy implied a number of zeros in this energy range but the actual zeroes were not evaluated.

V. IMPROVED STRUCTURE CONSTANT EVALUATION

The numerical work carried out so far strongly suggests that the approach using Eq. (50) is adequate for one ion per unit cell. However, for crystal structures with more than one ion per unit cell the maximum value of R is in general decreased. For example, if in our test fcc lattice, we considered the diamond structure, the maximum value of R is 2.7. Calculations with this value of R indicated poor convergence properties for the expansion coefficients. The problem arises, of course, for small values of I in Eqs. (62) and (63).

A possible solution to this problem as well as an improved one ion per unit cell calculation is based on a slightly altered expansion [cf. Eq. (54)],

$$\frac{1}{|\vec{k}+\vec{G}|^2 - E} = \sum_{m=0}^{N-1} (E+\lambda^2)^m \frac{1}{\left[|\vec{k}+\vec{G}|^2+\lambda^2\right]^{m+1}}$$

$$+ \frac{(E+\lambda^2)^N}{|\vec{k}+\vec{G}|^2 - E} \frac{1}{\left[|\vec{k}+\vec{G}|^2+\lambda^2\right]^N}, \tag{74}$$

where λ is arbitrary. We define the expansion coefficients BR, BI and Bl-4 just as in Eqs. (62) and (63), respectively, with the substitution

$$\left[|G+k|^2\right]^I \rightarrow \left[|G+k|^2 + \lambda^2\right]^I. \tag{75}$$

Corresponding changes also occur in the CX coefficients, Eq. (68).

For the larger values of m, we use exactly the same techniques as discussed above since convergence should be reasonably

rapid as long as λ^2 is not large compared to the lowest values of G^2. For the first few m values, say m = 0, 1, 2, we propose to calculate the expansion coefficient in coordinate space. We observe first that

$$\frac{1}{\left[\,|\vec{k}+\vec{G}|^2+\lambda^2\right]^2} = -\frac{1}{2\lambda}\frac{d}{d\lambda}\frac{1}{|\vec{k}+\vec{G}|^2+\lambda^2}, \qquad (76)$$

$$\frac{1}{\left[\,|\vec{k}+\vec{G}|^2+\lambda^2\right]^3} = \frac{1}{8\lambda^2}\left[\frac{d^2}{d\lambda^2}-\frac{1}{\lambda}\frac{d}{d\lambda}\right]\frac{1}{|\vec{k}+\vec{G}|^2+\lambda^2}. \qquad (77)$$

Next we equate the two representations for $H(\vec{R})$, Eqs. (33) and (22) [for negative energy $E = -\lambda^2$]

$$\frac{4\pi}{\Omega}\sum_{\vec{G}}\frac{e^{i(\vec{k}+\vec{G})\cdot(\vec{a}_\beta-\vec{a}_\alpha)}}{|\vec{k}+\vec{G}|^2+\lambda^2}e^{i(\vec{k}+\vec{G})\cdot\vec{R}}$$

$$= \sum_{N}e^{i\vec{k}\cdot\vec{R}_N}\frac{e^{-\lambda|\vec{R}_N+\vec{a}_\alpha-\vec{a}_\beta-\vec{R}|}}{|\vec{R}_N+\vec{a}_\alpha-\vec{a}_\beta-\vec{R}|} \qquad (78)$$

and make a $Y_{LM}(\hat{R})$ decomposition, leading to

$$\sum_{\vec{G}}\frac{e^{i(\vec{k}+\vec{G})\cdot(\vec{a}_\beta-\vec{a}_\alpha)}}{|\vec{k}+\vec{G}|^2+\lambda^2}j_L(|\vec{k}+\vec{G}|R)\,Y^*_{LM}(\widehat{\vec{k}+\vec{G}})$$

$$= \frac{\Omega}{4\pi}\left\{\frac{\lambda}{\sqrt{4\pi}}\frac{e^{-\lambda R}}{\lambda R}\delta_{\alpha\beta}\,\delta_{L0}\,\delta_{M0}\right. \qquad (79)$$

$$\left.+\frac{2}{\pi}\lambda i^{-L}\sum_{N}{}'e^{i\vec{k}\cdot\vec{R}_N}\tilde{I}_L(\lambda R)\tilde{K}_L(\lambda V)Y^*_{LM}(\hat{V})\right\},$$

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where the prime on the sum means the N = 0 term is deleted
if $\alpha = \beta$ and the vector $\vec{V}$ is

$$\vec{V} = \vec{R}_N + \vec{a}_\alpha - \vec{a}_\beta. \tag{80}$$

Multiplying by f(R) and integrating on R, we find an alter-
nate expression for BR(L, M, 1), namely,

$$BR(L,M,1) = \frac{\Omega}{4\pi} \left\{ \lambda \ \bar{H} \ \delta_{\alpha\beta} \ \delta_{L0} \ \delta_{M0} \right.$$

$$\left. + \frac{2}{\pi} \lambda \sum_N{}' P(L,M) \ H_L \ \tilde{K}_L(\lambda V) \ Re\left[\frac{1}{i^L} e^{i\vec{k}\cdot\vec{R}_N} e^{-iM\phi}\right] \right\}, \tag{81}$$

where ϕ is the azimuthal angle of the vector $\vec{V}$, H_L is given
in Eq. (70) with $x = \lambda V$ and $\bar{H}$ is the integral given in
Eq. (53) for E < 0 with $k_0 = \lambda$. The expression for BI(L,M,1)
is obvious, based on Eq. (81). B1-4(L,M,1) are somewhat more
complicated since they require the calculation in coordinate
space of both $\alpha = 1$, $\beta = 2$ and $\alpha = 2$, $\beta = 1$. Once the expres-
sions for I = 1 are derived, the results for I = 2 and I = 3
follow from Eqs. (76) and (77), respectively. These calcula-
tions are straightforward since the derivatives of $\tilde{I}_L$ and $\tilde{K}_L$
can be expressed in terms of modified spherical Bessel
functions.

The advantage of this scheme results from the fact that $\tilde{K}_L(x)$
falls off exponentially for large x. A few calculations for
selected values of L and M have been carried out with very
encouraging results. However, no detailed examination of this
scheme has yet been undertaken.

VI. CONCLUSIONS

What remains to be done to complete the initial model is
(1) to complete and thoroughly check out the computer program
for computing E vs $\vec{k}$; (2) to improve the calculation of $j_L(x)$
and $\tilde{I}_L(x)$ for small arguments; (3) to investigate further the
choice for μ [Eq. (56)] and the split between f_1 and f_2 as
a function of L; (4) to determine the sensitivity of E vs $\vec{k}$
as a function of errors in the structure constants and the
wave functions; (5) to investigate extensively the scheme
discussed in Section V; and (6) to sum over the bands to
calculate the total band energy.

Once the initial model is completed, tests of its usefulness
are needed, namely: (1) the calculation for a given volume
and lattice type must have a reasonable cost; (2) for a vari-
ety of known substances, the model must correctly predict the
stable crystal structure (note that this does not mean the
total cohesive energy need be calculated accurately, only that
the observed structure has the lowest energy according to our
model); (3) for known phase transitions at elevated pressures,
we should identify the fact that a phase transition occurs.
Note that this does not mean we could accurately predict at
what pressure the transition occurs--but only estimate it
approximately.

In applying these tests, we should be willing to be wrong
in some fraction of the cases, since the model is to serve
only as a guide for experiments. However, if the model
failed most of the tests, it will probably be necessary to
consider some or all of the ignored energy contributions,
and possibly even an improved ion potential.

APPENDIX

A crystal lattice is defined by its three primitive basis vectors, $\vec{a}$, $\vec{b}$ and $\vec{c}$. The possible relationships between these vectors fall into 14 categories, called Bravais lattices. As input to the computer program one prescribes the lattice type, the volume of a unit cell, Ω, and any needed length ratios. From this information, the primitive lattice vectors are calculated and from these the reciprocal lattice vectors, a*, b* and c*,

$$\vec{a}* = \frac{2\pi}{\Omega} \vec{b} \times \vec{c}, \quad \vec{b}* = \frac{2\pi}{\Omega} \vec{c} \times \vec{a}, \quad \vec{c}* = \frac{2\pi}{\Omega} \vec{a} \times \vec{b}. \qquad (A1)$$

A momentum space vector, $\vec{G}$, is then given by

$$\vec{G} = n_1 \vec{a}* + n_2 \vec{b}* + n_3 \vec{c}*, \qquad (A2)$$

while a direct lattice vector, $\vec{R}_N$, is given by

$$\vec{R}_N = N_1 \vec{a} + N_2 \vec{b} + N_3 \vec{c}.$$

Here, $\{n_1, n_2, n_3\}$ and $\{N_1, N_2, N_3\}$ are sets of three integers. For each ion in the unit cell, its charge (z_α), radius (ρ_α) and position ($\vec{a}_\alpha$) are specified. Here, $\alpha = 1, \ldots N$, with N being the total number (≤ 2) of ions in the unit cell.

A-1

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