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Ordering Energy and Effective Pairwise Interactions in a Binary Alloy of Simple Metals*†

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The pseudopotential theory of metals is applied to the case of a binary alloy with an arbitrary degree of order. A self-consistent screening potential which includes the effect of the total conduction-electron charge is derived to first order in a perturbation-theory expansion in the pseudopotential. Expressions are obtained for the conduction-electron contributions to the ordering energy and to the effective pairwise interactions among the ions in the alloy. If the conduction-electron energy may be expressed accurately to second order in the pseudopotential, this energy is shown to depend upon only two-particle correlations among the ion positions. Numerical values are obtained for the ordering energy and the pairwise interactions for stoichiometric LiMg. The ordering energy is not obviously inconsistent with experimental observations. If the ordering interaction is expressed approximately as a sum of two terms, one of which depends exponentially and the other sinusoidally on interionic separation, the former dominates throughout the region of the calculation.

I. INTRODUCTION

An attempt to extend the theory of metals to enable the calculation of properties of a binary alloy with an arbitrary degree of order is presented in this paper. In particular, expressions are obtained for the conduction-electron contributions to that portion of the crystalline energy which varies during rearrangements of the ions at constant volume, henceforth called the structure-dependent conduction-electron energy, and to the effective pairwise interactions among the ions. Numerical values are obtained for the difference in internal energy between the ordered and disordered states and for the pairwise interactions in a stoichiometric LiMg alloy.

The choice of the pseudopotential method for the treatment of the alloy problem presented in this work is motivated largely by the results of Harrison[1,2] and of Pick and Blandin.[3] These authors demonstrate that a consistent perturbation theory expansion of the electron energy in a periodic metal to second order in the potential yields a simple approximate expression for the structure-dependent conduction-electron energy. The accuracy of this expression is increased by the replacement of the actual potential with a suitable pseudopotential. A computation of the change in crystalline energy when the ions are rearranged at constant volume, such as occurs during the ordering of an alloy or a change of phase, is greatly simplified in this formalism by the avoidance of intermediate calculations of the band structure. Further, an effective pairwise interaction can be deduced from the expression for the structure-dependent conduction-electron energy. These related features indicate that the application of the pseudopotential method to the alloy problem, as suggested by Harrison[1] and by Pick and Sarma,[4] will yield appropriate expressions for the quantities of interest.

The conduction-electron contribution to the difference in internal energy between the ordered and completely disordered states is a significant alloy property which may be estimated from the structure-dependent conduction-electron energy. The importance of this contribution to the ordering energy was recognized by Mott[5] in his formulation of the polar model of an alloy. In this model, the actual interactions among the screened ions are approximated by the interactions between effective point charges located on each lattice site. The Thomas-Fermi model of the screening of an isolated Coulomb potential by an electron gas is used to compute the conduction-electron contribution to the effective point charges. Thus the effect of the electrons is reduced to that of point charges and the Madelung expression may be used to evaluate their contribution to the ordering energy. More recently, Harrison and Paskin[6] have reformulated the polar model in terms of an effective pairwise interaction between the ions in the alloy. They obtained an expression for this interaction using an asymptotic form of the screening density

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[1] W. A. Harrison, Phys. Rev. **129**, 2503 (1963); **129**, 2512 (1963).

[2] W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966), Chap. 3.

[3] R. Pick and A. Blandin, Physik Kondensierten Materie **3**, 1 (1964).

[4] R. Pick and G. Sarma, Phys. Rev. **135**, A1363 (1964).

[5] N. F. Mott, Proc. Phys. Soc. (London) **49**, 258 (1937).

[6] R. J. Harrison and A. Paskin, J. Phys. Radium **23**, 613 (1962).

derived by Langer and Vosko,[7] who considered the reaction of an electron gas to an isolated perturbing Coulomb potential. The electrons in the gas were allowed to interact with one another through a many-body potential. Unfortunately, their interaction is extremely sensitive to an adjustable parameter.

In the present work, an expression is obtained for the screening by an electron gas to first order in perturbation theory of a pseudopotential constructed from the potential of an isolated nonlocal Hartree-Fock ion. The electrons in the gas interact with one another through the Hartree potential only. While this treatment neglects the many-body interactions among the conduction electrons, it should represent the important interaction between the ions and the electrons more accurately than the other approaches. Expressions for the structure-dependent conduction-electron energy and for the effective pairwise interactions are derived in analogy with the procedure of Harrison[1] for single-element crystals. This approach to the alloy problem has the virtue of yielding an interaction which is free of adjustable parameters and which has, therefore, an unambiguous magnitude and shape.

II. FORMULATION OF THE ALLOY PROBLEM

The effective pairwise interactions among the ions in an alloy may be divided into two contributions. The first is the interaction which would remain if the ions were stripped of the conduction electrons. That is, it is the sum of the point ion Coulomb interaction, the van der Waals interaction, and the interaction due to core overlap. The latter two interactions are assumed to be small for the alloys being treated and are neglected in this formalism. The second contribution is the indirect interaction among the ions by means of the conduction-electron gas. This interaction depends upon the average electron density and may be derived for a given atomic volume from the structure-dependent conduction-electron energy, which will be denoted by E_{sd}.

By using a perturbation theory expansion of the electron energy with the set of plane waves as the zeroth-order wave functions, Harrison[1] found that E_{sd} could be approximated for a periodic metallic crystal by

$$E_{\mathrm{sd}}=\sum_{\{\mathbf{q}\}}{}' S(\mathbf{q})S^*(\mathbf{q})E(\mathbf{q})\,, \tag{1}$$

where

$$S(\mathbf{q})\equiv\sum_{\{\mathbf{R}\}}\frac{e^{-i\mathbf{q}\cdot\mathbf{R}}}{N}. \tag{2}$$

The set $\{\mathbf{R}\}$ consists of vectors to all of the ionic sites in the crystal from some convenient site chosen as origin. The structure factor, denoted by $S(\mathbf{q})$, is accordingly dependent upon only the positions of the ions, and not their nature. The energy–wave-number characteristic, denoted by $E(\mathbf{q})$, is dependent upon only the ionic potentials, the average electron density, and the atomic volume, and not the positions of the ions. Once $E(\mathbf{q})$ is evaluated for a given metal with a specified atomic volume, E_{sd} may be obtained for any crystalline structure from Eq. (1) without an intermediate calculation of the band structure. Accordingly, this formalism is well suited for obtaining the structure-dependent conduction-electron energy as a function of structure. By means of a comparison between Eq. (1) and the form of the expression for the energy of the point-ion interaction, Harrison deduced that the contribution of the indirect interaction to the effective pairwise interaction is

$$V_{II}(r)=\frac{\Omega_0}{\pi^2}\int_0^\infty dq\, q^2E(q)\frac{\sin qr}{qr}\,, \tag{3}$$

where Ω_0 is the volume per ion. Thus the indirect interaction follows immediately from a knowledge of the energy–wave-number characteristic.

In order to obtain Eqs. (1) and (3) from the perturbation theory expansion of the energy, it is necessary to neglect all terms which are of higher order than second in the pseudopotential. By the introduction of additional structure dependence, these higher-order terms would prevent the expression of E_{sd} in the simple form of Eq. (1) and thereby prevent the deduction of a structure-independent effective pairwise interaction. The retention of terms of higher order than second in the pseudopotential would introduce the same complications in the problem considered here. Since the goal of this work is to obtain information about the changes in the energy of the alloy system in response to changes in the ionic arrangement at constant volume, within a formalism which leads to a structure-independent effective pairwise interaction, these higher-order terms are neglected here.

We now proceed with a derivation which follows the pseudopotential formalism of Harrison[1,2,8] for periodic crystals whenever it is appropriate. E_{sd} depends upon the conduction-electron eigenstates of the nonlocal one-electron crystalline Hamiltonian,

$$H=T+V^I+V^{SC}, \tag{4}$$

where

$$\langle\mathbf{r}|T|\mathbf{r}'\rangle\equiv(-\nabla_{\mathbf{r}}\cdot\nabla_{\mathbf{r}}+\bar{V}_L)\delta(\mathbf{r}-\mathbf{r}'). \tag{5}$$

Throughout this work, atomic units are used for all quantities except energies, which are in rydbergs. $\bar{V}_L$ is the spatial average of the Hartree potentials of all the ions and conduction electrons in the crystal. V^I is the sum of the Hartree-Fock potentials of all the ions less the spatial average of the Hartree potentials. In the absence of a suitable method for including the effects of both exchange and correlation among the conduction electrons in a unified formalism, we will approximate

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[7] J. S. Langer and S. H. Vosko, J. Phys. Chem. Solids 12, 196 (1959).

[8] Reference 2, Chaps. 2 and 8.

V^{SC} with the Hartree potential of the conduction electron gas less the spatial average of that potential. The basis functions for the perturbation theory which follows are eigenfunctions of the operator T, the set of plane waves. The wave function of the plane-wave state $\mathbf{k}$ is given by

$$\langle \mathbf{r}|\mathbf{k}\rangle \equiv \exp(i\mathbf{k}\cdot\mathbf{r})/\Omega^{1/2}, \tag{6}$$

where Ω is the volume of the crystal, and the associated eigenvalue of T is $k^2+\bar{V}_L$.

In applying the pseudopotential method to a given system, each electron state is labeled as either a core state, denoted by c, or a valence (conduction-electron) state, denoted by v. In this problem, the core states are those states whose eigenfunctions are sufficiently localized about their respective nuclei that they may be very closely approximated by the corresponding atomic eigenfunctions. We then adopt the pseudopotential formalism of Austin, Heine, and Sham,[9] who established the properties of a general pseudo-Hamiltonian, $H_p \equiv T+W$, where the pseudopotential, denoted by W, is defined by

$$W \equiv V^I + V^{SC} + V^R. \tag{7}$$

The repulsive potential, denoted by V^R, is defined by the relation

$$\langle \mathbf{r}|V^R|\mathbf{r}'\rangle \equiv \sum_c \langle \mathbf{r}|c\rangle f_c(\mathbf{r}'), \tag{8}$$

where the sum extends over all the core states of H. $f_c(\mathbf{r}')$ represents an arbitrary function of $\mathbf{r}'$ and the parameter c. The essential properties of the eigenstates of H_p result directly from the exclusion of the valence states from the sum in Eq. (8) and may be summarized as follows: The "core" eigenstates of H_p are linear combinations of the core eigenstates of H; the "valence" eigenvalues of H_p are identical with the valence eigenvalues of H; the "valence" eigenstates of H_p, denoted by $\bar{v}$, are related to the valence eigenstates of H by

$$|v\rangle = |\bar{v}\rangle - \sum_c |c\rangle\langle c|\bar{v}\rangle. \tag{9}$$

A pseudopotential is constructed by selecting a particular form for $f_c(\mathbf{r}')$, which might be an operator or an energy-dependent expression. In general, $f_c(\mathbf{r}')$ is chosen to optimize in some sense the convergence of a procedure for determining the conduction-electron property of interest. For instance, it is desirable in this problem to optimize the convergence of a perturbation theory expansion of the total conduction-electron energy in orders of the pseudopotential using a basis set of plane waves. However, we will proceed with the derivation using the general form of the pseudopotential given by Eqs. (7) and (8).

The unscreened pseudopotential, denoted by W^0 and equal to V^I+V^R, is examined first. V^I is determined by the Hartree-Fock potentials of the ion cores, which consist of the nuclei plus those electrons which occupy core states. We have assumed that the core eigenfunctions may be very closely approximated by the corresponding atomic eigenfunctions. This assumption is justified only if the core eigenfunctions are sufficiently localized about the nuclei that the difference between the crystalline and atomic potentials may be considered as essentially constant over the core region. Under these conditions, the ionic Hartree-Fock potential for an A ion, for instance, in an AB alloy will be independent of the lattice site occupied by that ion since it depends upon only the nuclear charge and the core eigenfunctions. Taking advantage of this invariance and the definition

$$\begin{aligned} \sigma(\mathbf{R}) &= +1 \text{ if the site } \mathbf{R} \text{ contains an } A \text{ ion},\\ \sigma(\mathbf{R}) &= -1 \text{ if the site } \mathbf{R} \text{ contains a } B \text{ ion}, \end{aligned} \tag{10}$$

we may write

$$\begin{aligned} \langle \mathbf{r}|\bar{V}_L{}^I + V^I|\mathbf{r}'\rangle = \tfrac{1}{2}\sum_{\{\mathbf{R}\}} \{&[1+\sigma(\mathbf{R})]\langle \mathbf{r}-\mathbf{R}|v_A|\mathbf{r}'-\mathbf{R}\rangle \\ &+[1-\sigma(\mathbf{R})]\langle \mathbf{r}-\mathbf{R}|v_B|\mathbf{r}'-\mathbf{R}\rangle\}. \end{aligned} \tag{11}$$

Here, v_i is the Hartree-Fock potential of an ion of type i and $\bar{V}_L{}^I$ is the spatial average of the Hartree potential of the array of ions.

As expressed in Eq. (11), $\bar{V}_L{}^I + V^I$ has a general form which occurs repeatedly throughout this work. Let us consider a general function G which can be expressed for a given configuration of ions in the AB alloy in terms of a sum over ionic functions g_i as

$$\begin{aligned} \langle \mathbf{r}|G|\mathbf{r}'\rangle = \tfrac{1}{2}\sum_{\{\mathbf{R}\}} \{&[1+\sigma(\mathbf{R})]\langle \mathbf{r}-\mathbf{R}|g_A|\mathbf{r}'-\mathbf{R}\rangle \\ &+[1-\sigma(\mathbf{R})]\langle \mathbf{r}-\mathbf{R}|g_B|\mathbf{r}'-\mathbf{R}\rangle\}. \end{aligned} \tag{12}$$

This form merely expresses the property that the function g_i which is associated with an ion of type i is independent of the lattice site occupied by that ion. A matrix element of G between the plane-wave basis functions can be written as

$$\begin{aligned} \langle \mathbf{k}+\mathbf{q}|G|\mathbf{k}\rangle = \tfrac{1}{2}\sum_{\{\mathbf{R}\}} e^{-i\mathbf{q}\cdot\mathbf{R}}\{&[1+\sigma(\mathbf{R})]\langle \mathbf{k}+\mathbf{q}|g_A|\mathbf{k}\rangle \\ &+[1-\sigma(\mathbf{R})]\langle \mathbf{k}+\mathbf{q}|g_B|\mathbf{k}\rangle\}. \end{aligned} \tag{13}$$

It is convenient to define an average g by

$$\begin{aligned} \langle \mathbf{k}+\mathbf{q}|\bar{g}|\mathbf{k}\rangle \equiv{}& xN\langle \mathbf{k}+\mathbf{q}|g_A|\mathbf{k}\rangle \\ &+(1-x)N\langle \mathbf{k}+\mathbf{q}|g_B|\mathbf{k}\rangle \end{aligned} \tag{14}$$

and a difference g by

$$\langle \mathbf{k}+\mathbf{q}|\Delta g|\mathbf{k}\rangle \equiv \tfrac{1}{2}N\langle \mathbf{k}+\mathbf{q}|g_A|\mathbf{k}\rangle - \tfrac{1}{2}N\langle \mathbf{k}+\mathbf{q}|g_B|\mathbf{k}\rangle, \tag{15}$$

as well as

$$\langle \sigma\rangle_R \equiv \sum_{\{\mathbf{R}\}} \frac{\sigma(\mathbf{R})}{N} = 2x-1, \tag{16}$$

where N is the number of atoms in the crystal and x is

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[9] B. J. Austin, V. Heine, and L. J. Sham, Phys. Rev. **127**, 276 (1962).

the fraction of them which are of type A. Substitution of Eqs. (2), (14), (15), and (16) into Eq. (13) yields

$$\langle \mathbf{k}+\mathbf{q}|G|\mathbf{k}\rangle = S(\mathbf{q})\langle \mathbf{k}+\mathbf{q}|\bar{g}|\mathbf{k}\rangle + F(\mathbf{q})\langle \mathbf{k}+\mathbf{q}|\triangle g|\mathbf{k}\rangle\,, \tag{17}$$

where

$$F(\mathbf{q}) \equiv \sum_{\{\mathbf{R}\}} \frac{e^{-i\mathbf{q}\cdot\mathbf{R}}}{N}[\sigma(\mathbf{R}) - \langle\sigma\rangle_R]\,. \tag{18}$$

The significance of Eq. (17) is not readily apparent on the basis of a cursory inspection. However, the vanishing of $S(\mathbf{q})F^*(\mathbf{q})$ for all values of $\mathbf{q}$ is easily demonstrated using Eq. (16). In the common case of an alloy such that the vectors $\{\mathbf{R}\}$ form a Bravais lattice, the set of reciprocal space vectors, $\{\mathbf{q}\}$, can be divided into two subsets. These are the reciprocal-lattice vectors $\{\mathbf{K}\}$, which have the property that $\exp(-i\mathbf{K}\cdot\mathbf{R})=1$ for all members of $\{\mathbf{R}\}$, and all other reciprocal vectors. It is easily shown that $S(\mathbf{q})=\Delta(\mathbf{q},\mathbf{K})$, where $\Delta(\mathbf{q},\mathbf{K})$ is equal to unity if $\mathbf{q}$ is a reciprocal-lattice vector and zero otherwise. For such an alloy, it follows that $F(\mathbf{K})=0$. However, for any alloy structure, the important consequence of the vanishing of $S(\mathbf{q})F^*(\mathbf{q})$ is that only one of the two terms on the right-hand side of Eq. (17) is nonzero for any point $\mathbf{q}$. Thus, a given matrix element of G is always the product of a g_i-independent factor, such as $F(\mathbf{q})$ or $S(\mathbf{q})$, and a structure-independent factor, such as a matrix element of $\bar{g}$ or $\triangle g$. This separability, when demonstrated for the screened pseudopotential, will lead directly to structure-independent energy–wave-number characteristics and effective pairwise interactions. Having demonstrated the form for $\bar{V}_L{}^I + V^I$ through the analogy between Eqs. (11) and (12), we now proceed to show that the other term in the unscreened pseudopotential, V^R, can be similarly described.

The repulsive potential, as defined in Eq. (8), can be written more explicitly as

$$\langle \mathbf{r}|V^R|\mathbf{r}'\rangle = \sum_{\{\mathbf{R}\}}\sum_{nlms} \langle \mathbf{r}-\mathbf{R}|nlms;\mathbf{R}\rangle f_{nlms;\mathbf{R}}(\mathbf{r}'-\mathbf{R})\,. \tag{19}$$

Here, n, l, m, and s are the usual radial, orbital, and spin quantum numbers used to describe one-electron ionic core states. The assumed invariance of the core eigenfunctions is typical of the invariance which must characterize other components of the pseudopotential in order that separability be achieved. Accordingly, we find it necessary to restrict the very general form of the $f_c(\mathbf{r}')$ so that the $f_c(\mathbf{r}')$ associated with a particular type of ion is independent of the surroundings of that ion. While this requirement is not an assumption in any sense, it does limit the freedom which one has, in principle, to optimize the convergence of the perturbation expansion by variations of $f_c(\mathbf{r}')$. With this restriction, Eq. (19) can be written in the form of Eq. (12). It is convenient to define the unscreened pseudopotential associated with an ion of type i located at the origin by

$$\langle \mathbf{r}|w_i{}^0|\mathbf{r}'\rangle \equiv \langle \mathbf{r}|v_i|\mathbf{r}'\rangle + \sum_{nlms} \langle \mathbf{r}|nlms;i\rangle f_{nlms;i}(\mathbf{r}')\,. \tag{20}$$

Replacing G by $\bar{V}_L{}^I + W^0$, $\bar{g}$ by $\bar{w}^0$, and $\triangle g$ by $\triangle w^0$, the same analysis which yielded Eq. (17) from Eq. (12) leads to the relation

$$\langle \mathbf{k}+\mathbf{q}|\bar{V}_L{}^I + W^0|\mathbf{k}\rangle = S(\mathbf{q})\langle \mathbf{k}+\mathbf{q}|\bar{w}^0|\mathbf{k}\rangle + F(\mathbf{q})\langle \mathbf{k}+\mathbf{q}|\triangle w^0|\mathbf{k}\rangle\,. \tag{21}$$

Since the difference unscreened pseudopotential $\triangle w^0$ vanishes in the limit in which the two types of atoms are identical, Eq. (21) reduces to the appropriate unscreened pseudopotential for an elemental crystal.

The above expression for the matrix elements of the unscreened pseudopotential may be discussed in relation to the virtual crystal approximation, which has been used widely to treat the case of a completely disordered binary alloy. In this approximation, the actual potential due to the ions in the crystal is replaced by a periodic array of effective ionic potentials. This effective potential is the weighted average of the two different ionic potentials in the alloy. As may readily be verified by examining the definition of the average g in Eq. (14), the first term on the right-hand side of Eq. (21) represents a virtual crystal approximation for the potential of the pseudo-ions. This term depends primarily upon the configuration of ionic states in the crystal, rather than the arrangement of the ions on the sites. The second term is a correction to the virtual crystal approximation which accounts for the difference between the ionic potentials and depends in detail upon the arrangement of the ions on the ionic sites. This term is nonvanishing for all ionic configurations. Further, it must be stressed that $S(\mathbf{q})$ and $F(\mathbf{q})$ do not necessarily contain all of the structure dependence in Eq. (21). As defined above, the average and difference unscreened pseudopotentials are not strictly independent of the structure, but can vary with the ionic arrangement through variations in the optimal $f_c(\mathbf{r})$. For the calculation of certain physical quantities, such as the effective pairwise interactions, we have found it convenient to restrict $f_c(\mathbf{r})$ to being invariant under rearrangements of the ions at constant volume. Under that restriction, the average and difference unscreened pseudopotentials are truly constant during variations of that sort. In any case, it is expected that the ordering process will affect the pseudopotential most strongly through variations in $F(\mathbf{q})$, not $f_c(\mathbf{r})$. This expectation has been borne out in calculations on LiMg. Let us now turn to the calculation of the matrix elements of the screening potential.

In the Hartree approximation, Poisson's equation may be used to express the relationship between the matrix elements of the screening potential and the matrix elements of the conduction-electron density in a basis of plane waves. Since V^{SC} is manifestly local in this approximation, its matrix elements are a function only of the difference between the wave vectors. If n is the conduction-electron density operator, the off-diagonal matrix elements of V^{SC} may be written as

$$\langle \mathbf{q}|V^{SC}|0\rangle = \frac{8\pi}{|\mathbf{q}|^2}\langle \mathbf{q}|n|0\rangle, \tag{22}$$

where

$$\langle \mathbf{r}|n|\mathbf{r}'\rangle \equiv \sum_{\{v\}} |\langle \mathbf{r}|v\rangle|^2 \delta(\mathbf{r}-\mathbf{r}'). \tag{23}$$

The set $\{v\}$ consists of the occupied valence eigenstates of H.[9a] Using Eq. (9), $|\langle \mathbf{r}|v\rangle|^2$ may be written as

$$|\langle \mathbf{r}|v\rangle|^2 = |\langle \mathbf{r}|\bar{v}\rangle|^2 - 2\,\mathrm{Re}(\langle \mathbf{r}|P|\bar{v}\rangle\langle\bar{v}|\mathbf{r}\rangle) + \langle \mathbf{r}|P|\bar{v}\rangle\langle\bar{v}|P|\mathbf{r}\rangle, \tag{24}$$

where $\bar{v}$ satisfies the pseudo-Hamiltonian equation,

$$H_p|\bar{v}\rangle = T|\bar{v}\rangle + W|\bar{v}\rangle = E_v|\bar{v}\rangle, \tag{25}$$

and the crystalline core projection operator, denoted by P, is defined by

$$\langle \mathbf{k}+\mathbf{q}|P|\mathbf{k}\rangle \equiv \sum_c \langle \mathbf{k}+\mathbf{q}|c\rangle\langle c|\mathbf{k}\rangle. \tag{26}$$

It is now shown that Eq. (22) can be written in the separated form of Eq. (17). By analogy with the application of the pseudopotential method to a single-element crystal,[8] it may be assumed that all terms of order higher than first in the pseudopotential must be neglected in the plane-wave perturbation theory expansion of the right-hand side of Eq. (22). Our examination of alternative procedures indicates that this assumption is justified. Accordingly, let us associate the state $\bar{v}$ with the zeroth-order wave function, $a_0(\mathbf{k})|\mathbf{k}\rangle$. This association does not imply that $\mathbf{k}$ is a good quantum number in the alloy. Expansion of the wave function of $\bar{v}$ in plane waves and neglect of all contributions to the wave function involving the product of two or more matrix elements of the pseudopotential yields

$$|\bar{v}\rangle = a_0(\mathbf{k})\left(|\mathbf{k}\rangle + \sum_{\{\mathbf{q}\}}{}' |\mathbf{k}+\mathbf{q}\rangle \frac{\langle \mathbf{k}+\mathbf{q}|W|\mathbf{k}\rangle}{|\mathbf{k}|^2 - |\mathbf{k}+\mathbf{q}|^2}\right). \tag{27}$$

In writing this equation, we have ignored the vanishing of the denominator for certain values of $\mathbf{q}\neq 0$. The difficulty encountered in the evaluation of expressions involving such a singularity has been closely examined by Harrison[2] and by Pick and Blandin.[3] They conclude that this singularity enters into a perturbation theory expression for the total conduction-electron energy accurate to second order in the pseudopotential only in the form

$$\int_{k_F} d\mathbf{k} \frac{h(\mathbf{k})}{|\mathbf{k}|^2 - |\mathbf{k}+\mathbf{q}|^2}, \tag{28}$$

where the integral extends over the Fermi sphere of radius k_F and $h(\mathbf{k})$ is a slowly varying function of $\mathbf{k}$ everywhere. The principal value of this integral is a well-defined function for all values of $\mathbf{q}\neq 0$, independent of the relationship between q and k_F. These results are fully applicable to the alloy problem. Hence, it may be concluded that, whereas the singularity occurring in Eq. (27) leads in many instances to insurmountable difficulties in the evaluation of properties of individual electron eigenstates, such as the energy or the wave function, properties derivable from the second-order perturbation theory expression for the total conduction-electron energy can be evaluated without any particular difficulties. It must be pointed out, however, that there may be physical properties, including the energies, of certain alloy systems whose perturbation theory expansions are strongly influenced by terms of order higher than second in the pseudopotential. In these instances, the second-order expression for the conduction-electron energy can be readily evaluated but will be of little significance. The formation of a long-period superlattice in an alloy may be an example of such a process.

Ignoring the singularity in the perturbation theory expression, Eq. (27) may be substituted into Eq. (24) to obtain

$$\begin{aligned}|\langle \mathbf{r}|v\rangle|^2 &= |a_0(\mathbf{k})|^2 [|\langle \mathbf{r}|\mathbf{k}\rangle|^2 \\ &\quad - 2\,\mathrm{Re}(\langle \mathbf{r}|P|\mathbf{k}\rangle\langle \mathbf{k}|\mathbf{r}\rangle) + \langle \mathbf{r}|P|\mathbf{k}\rangle\langle \mathbf{k}|P|\mathbf{r}\rangle] \\ &\quad + 2|a_0(\mathbf{k})|^2\,\mathrm{Re}\Bigg[\sum_{\{\mathbf{q}\}}{}' \frac{\langle \mathbf{k}+\mathbf{q}|W|\mathbf{k}\rangle}{|\mathbf{k}|^2 - |\mathbf{k}+\mathbf{q}|^2} \\ &\quad \times (\langle \mathbf{r}|\mathbf{k}+\mathbf{q}\rangle\langle \mathbf{k}|\mathbf{r}\rangle - \langle \mathbf{r}|P|\mathbf{k}+\mathbf{q}\rangle\langle \mathbf{k}|\mathbf{r}\rangle \\ &\quad - \langle \mathbf{r}|\mathbf{k}+\mathbf{q}\rangle\langle \mathbf{k}|P|\mathbf{r}\rangle + \langle \mathbf{r}|P|\mathbf{k}+\mathbf{q}\rangle\langle \mathbf{k}|P|\mathbf{r}\rangle)\Bigg]. \end{aligned} \tag{29}$$

To obtain an expression for $|a_0(\mathbf{k})|^2$, both sides of Eq. (29) are integrated over the crystalline volume. The resulting left-hand side is unity since the state v contains just one electron. Therefore, $|a_0(\mathbf{k})|^2$ is given by

$$|a_0(\mathbf{k})|^2 = \Bigg[1 - \langle \mathbf{k}|P|\mathbf{k}\rangle - 2\,\mathrm{Re}\left(\sum_{\{\mathbf{q}\}}{}' \frac{\langle \mathbf{k}|P|\mathbf{k}+\mathbf{q}\rangle\langle \mathbf{k}+\mathbf{q}|W|\mathbf{k}\rangle}{|\mathbf{k}|^2 - |\mathbf{k}+\mathbf{q}|^2}\right)\Bigg]^{-1}. \tag{30}$$

This expression for $|a_0(\mathbf{k})|^2$ is dependent upon the matrix elements of the screening potential for all nonzero values of $\mathbf{q}$ through the presence of the matrix elements of the pseudopotential. Accordingly, if this expression were used in a calculation of the matrix elements of V^{SC}, a given matrix element of the screening density defined in Eq. (23), and hence a given matrix element of V^{SC} as given in Eq. (22), would also depend upon all the matrix elements of V^{SC}. This would be

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[9a] *Note added in proof.* While the formal lack of orthogonality among the members of $\{v\}$ as obtained through Eq. (9) has been ignored in the writing of Eq. (23), we have found that this nonorthogonality does not affect the screening to first order in the pseudopotential.

true even if Eq. (29) were linearized after the substitution of Eq. (30). Therefore, the matrix elements of the screening potential would result only from the solution of an infinite set of equations. In addition, and of more significance in this treatment, the resulting matrix elements of V^{SC} would not have the proper form to enable the separation of the matrix elements of W. In order to avoid this situation, we shall introduce the approximation that the matrix elements of the crystalline core projection operator, P, may be treated as first-order expressions in W. This approximation is discussed in detail by Harrison.[8] The small magnitude of the matrix elements of P, typically of order 0.1, suggests that the approximation is reasonable.

As a result of this approximation, $|a_0(\mathbf{k})|^2$ can be written to "first order" in the pseudopotential as

$$|a_0(\mathbf{k})|^2=(1-\langle\mathbf{k}|P|\mathbf{k}\rangle)^{-1}. \tag{31}$$

In order to find the matrix elements of the screening density, the matrix elements of Eq. (29) must be evaluated in a basis of plane waves. This leads to expressions like

$$\sum_c\sum_{c'}\langle\mathbf{k}+\mathbf{q}'|c\rangle\int_\Omega d\mathbf{r}\langle c|\mathbf{r}\rangle e^{-i\mathbf{q}\cdot\mathbf{r}}\langle\mathbf{r}|c'\rangle\langle c'|\mathbf{k}\rangle, \tag{32}$$

where the sum over core states in P has been displayed explicitly. If $\mathbf{q}=0$, the orthonormality of the core states reduces this expression to a matrix element of P. The presence of $\exp(-i\mathbf{q}\cdot\mathbf{r})$ in the integral serves to moderate the sharp orthonormality condition and should not increase markedly the magnitude of the expression. Accordingly, we shall also consider expressions like (32) to be "first order" in the pseudopotential. With these approximations, the matrix elements of the screening density may be evaluated and Eq. (22) used to write the matrix elements of V^{SC} to first order in W^0 as

$$\langle\mathbf{q}|V^{SC}|0\rangle=\frac{8\pi}{\Omega|\mathbf{q}|^2}\frac{1}{D(\mathbf{q})}\sum_{\{\mathbf{k}\}_F}|a_0(\mathbf{k})|^2\times\left(\frac{\langle\mathbf{k}+\mathbf{q}|W^0|\mathbf{k}\rangle}{|\mathbf{k}|^2-|\mathbf{k}+\mathbf{q}|^2}+\frac{\langle\mathbf{k}-\mathbf{q}|W^0|\mathbf{k}\rangle^*}{|\mathbf{k}|^2-|\mathbf{k}-\mathbf{q}|^2}+B(\mathbf{k},\mathbf{q})\right), \tag{33}$$

where

$$D(\mathbf{q})\equiv1-\frac{8\pi}{\Omega|\mathbf{q}|^2}\sum_{\{\mathbf{k}\}_F}|a_0(\mathbf{k})|^2\times\left(\frac{1}{|\mathbf{k}|^2-|\mathbf{k}+\mathbf{q}|^2}+\frac{1}{|\mathbf{k}|^2-|\mathbf{k}-\mathbf{q}|^2}\right) \tag{34}$$

and

$$B(\mathbf{k},\mathbf{q})\equiv-\langle\mathbf{k}+\mathbf{q}|P|\mathbf{k}\rangle-\langle\mathbf{k}|P|\mathbf{k}-\mathbf{q}\rangle+\int_\Omega d\mathbf{r}\langle\mathbf{k}|P|\mathbf{r}\rangle e^{-i\mathbf{q}\cdot\mathbf{r}}\langle\mathbf{r}|P|\mathbf{k}\rangle. \tag{35}$$

The sum over $\{v\}$ of Eq. (23) has been replaced in these expressions by an equivalent sum over the set of states, denoted by $\{\mathbf{k}\}_F$, contained within the Fermi volume.

It is apparent from the form of Eq. (33) and the separability of W^0 that the separability of V^{SC}, as discussed in connection with G, will follow directly from the separability of $B(\mathbf{k},\mathbf{q})$ if $|a_0(\mathbf{k})|^2$ is independent of the arrangement of the ions in the alloy. To show this independence, the invariance of the core states is used to write the $\mathbf{r}$-space representation of P as

$$\langle\mathbf{r}|P|\mathbf{r}'\rangle=\tfrac{1}{2}\sum_{\{\mathbf{R}\}}\{[1+\sigma(\mathbf{R})]\langle\mathbf{r}-\mathbf{R}|p_A|\mathbf{r}'-\mathbf{R}\rangle+[1-\sigma(\mathbf{R})]\langle\mathbf{r}-\mathbf{R}|p_B|\mathbf{r}'-\mathbf{R}\rangle\}, \tag{36}$$

where the projection operator associated with an ion of type i at the origin is given by

$$\langle\mathbf{r}|p_i|\mathbf{r}'\rangle\equiv\sum_{nlms}\langle\mathbf{r}|nlms;\,i\rangle\langle i;\,nlms|\mathbf{r}'\rangle. \tag{37}$$

In strict analogy with the treatment of G, the matrix elements of P may be written as

$$\langle\mathbf{k}+\mathbf{q}|P|\mathbf{k}\rangle=S(\mathbf{q})\langle\mathbf{k}+\mathbf{q}|\bar{p}|\mathbf{k}\rangle+F(\mathbf{q})\langle\mathbf{k}+\mathbf{q}|\Delta p|\mathbf{k}\rangle. \tag{38}$$

Since $|a_0(\mathbf{k})|^2$ depends only upon $\langle\mathbf{k}|P|\mathbf{k}\rangle$, Eq. (38) demonstrates that it depends only upon $\langle\mathbf{k}|\bar{p}|\mathbf{k}\rangle$ and is, therefore, independent of the arrangement of the ions in the crystal. It does, however, depend upon the relative numbers of A and B ions.

To establish the separability of $B(\mathbf{k},\mathbf{q})$, we note that the assumption that the core states are invariant is reasonable only if the overlap of core wave functions on adjacent ions is negligible. Accordingly, the middle integral in the last sum of Eq. (35) must vanish unless c and c' are associated with the same ion. This property implies that this sum may be written as

$$\tfrac{1}{2}\sum_{\{\mathbf{R}\}}\{[1+\sigma(\mathbf{R})]\int_\Omega d\mathbf{r}\langle\mathbf{k}|p_A|\mathbf{r}-\mathbf{R}\rangle\times e^{-i\mathbf{q}\cdot\mathbf{r}}\langle\mathbf{r}-\mathbf{R}|p_A|\mathbf{k}\rangle+[1-\sigma(\mathbf{R})]\times\int_\Omega d\mathbf{r}\langle\mathbf{k}|p_B|\mathbf{r}-\mathbf{R}\rangle e^{-i\mathbf{q}\cdot\mathbf{r}}\langle\mathbf{r}-\mathbf{R}|p_B|\mathbf{k}\rangle\}. \tag{39}$$

We will now define an ionic $b_i(\mathbf{k},\mathbf{q})$ by

$$b_i(\mathbf{k},\mathbf{q})\equiv-\langle\mathbf{k}+\mathbf{q}|p_i|\mathbf{k}\rangle-\langle\mathbf{k}|p_i|\mathbf{k}-\mathbf{q}\rangle+\int_\Omega d\mathbf{r}\langle\mathbf{k}|p_i|\mathbf{r}\rangle e^{-i\mathbf{q}\cdot\mathbf{r}}\langle\mathbf{r}|p_i|\mathbf{k}\rangle \tag{40}$$

and proceed in analogy with our treatment of G to write

$$B(\mathbf{k},\mathbf{q})=S(\mathbf{q})\bar{b}(\mathbf{k},\mathbf{q})+F(\mathbf{q})\Delta b(\mathbf{k},\mathbf{q}). \tag{41}$$

Here, $\bar{b}$ and Δb are defined in strict analogy with Eqs. (14) and (15).

Since $|a_0(\mathbf{k})|^2$ is independent of the ionic arrangement and $B(\mathbf{k},\mathbf{q})$ can be written as in Eq. (41), $\langle\mathbf{q}|V^{SC}|0\rangle$ depends directly upon the ionic arrangement only through a factor of either $S(\mathbf{q})$ or $F(\mathbf{q})$, whichever is nonvanishing for that value of $\mathbf{q}$. Of course, the matrix elements of the screening potential may also depend upon the ionic arrangement indirectly through the optimal form for $f_c(\mathbf{r})$. In any case, the matrix elements of V^{SC} can be separated in the same manner as were those of W^0. By defining an average screening potential by

$$\langle\mathbf{q}|\bar{v}^{SC}|0\rangle\equiv\frac{8\pi}{\Omega|\mathbf{q}|^2D(\mathbf{q})}\sum_{\{\mathbf{k}\}F}|a_0(\mathbf{k})|^2 \times\left[\frac{\langle\mathbf{k}+\mathbf{q}|\bar{w}^0|\mathbf{k}\rangle}{|\mathbf{k}|^2-|\mathbf{k}+\mathbf{q}|^2}+\frac{\langle\mathbf{k}-\mathbf{q}|\bar{w}^0|\mathbf{k}\rangle^*}{|\mathbf{k}|^2-|\mathbf{k}-\mathbf{q}|^2}+\bar{b}(\mathbf{k},\mathbf{q})\right] \tag{42}$$

and a difference screening potential in a completely analogous manner, the matrix elements of the screening potential can be written as

$$\langle\mathbf{q}|V^{SC}|0\rangle=S(\mathbf{q})\langle\mathbf{q}|\bar{v}^{SC}|0\rangle+F(\mathbf{q})\langle\mathbf{q}|\Delta v^{SC}|0\rangle. \tag{43}$$

This expression for V^{SC} differs from that obtained by Harrison[8] in two respects. Since he chose to treat the conduction-electron charge which arises from the sum over core states in Eq. (9) as part of an effective valence, there is no contribution in his expression from terms analogous to $B(\mathbf{k},\mathbf{q})$. In addition, $|a_0(\mathbf{k})|^2$ has been set equal to unity. While it may be argued that setting $|a_0(\mathbf{k})|^2=1$ does not drop any terms from Eq. (42) which are not of second or higher order in the pseudopotential, we have chosen to retain both this contribution and that from $B(\mathbf{k},\mathbf{q})$. For the system LiMg, $|a_0(\mathbf{k})|^2$ increases the matrix elements of the screening potential by 6 to 8% for important values of $\mathbf{q}$. The terms resulting from $B(\mathbf{k},\mathbf{q})$ decrease the screening potential matrix elements by about 0.5% for $q=0.25$ atomic units (a.u.) and by 20 to 30% for $q=1.50$ a.u. Therefore, the combined effect of the two corrections tends to redistribute the screening potential in $\mathbf{q}$ space. By combining Eq. (21) with Eq. (42), the matrix elements of the total screened pseudopotential can be written as

$$\langle\mathbf{k}+\mathbf{q}|\bar{V}_L+W|\mathbf{k}\rangle=S(\mathbf{q})\langle\mathbf{k}+\mathbf{q}|\bar{w}|\mathbf{k}\rangle +F(\mathbf{q})\langle\mathbf{k}+\mathbf{q}|\Delta w|\mathbf{k}\rangle, \tag{44}$$

where

$$\bar{w}\equiv\bar{w}^0+\bar{v}^{SC} \quad\text{and}\quad \Delta w\equiv\Delta w^0+\Delta v^{SC}.$$

Having obtained a separated form for the screened pseudopotential, we shall review the assumptions which were required to achieve this form. In this use of the Austin, Heine, and Sham[9] form of the pseudopotential, the core eigenfunctions are assumed to be closely approximated by the corresponding atomic wave functions and, accordingly, to be independent of the local environment of the ion. Use is made of the implication of this assumption that the core eigenfunctions on adjacent ions in the solid do not overlap. It is also assumed that the Hartree-Fock one-electron Hamiltonian is sufficient to describe the interaction of the conduction-electron eigenstates with the core-electron eigenstates. These assumptions are common to most orthogonalized-plane-wave (OPW) and pseudopotential approaches. In addition, the form of $f_c(\mathbf{r})$ is restricted in this treatment to one which does not vary among the ions of one type throughout the alloy, for a particular configuration of ions. This last restriction is, of course, trivial in the case of a periodic elemental crystal. While this restriction enabled the separation of W^0, it must be remembered that the matrix elements of $\bar{w}^0$ and Δw^0 may depend upon the arrangement of the ions through $f_c(\mathbf{r})$. Perturbation theory is used to obtain an expression for V^{SC} in the Hartree approximation which is first order in the pseudopotential. Finally, by assuming that the matrix elements of the crystalline core projection operator may be treated as first-order expressions in the pseudopotential, we were able to separate the matrix elements of V^{SC}, and therefore of W.

Turning to a discussion of the crystalline energy, it is convenient to distinguish two groups of charges. The first group consists of the ionic cores, while the second consists of the conduction electrons. By the conduction-electron contribution to the crystalline energy, we mean the self-energy of the second group of charges plus the energy of interaction between the first and second groups. Summing the energy E_v over all of the occupied conduction-electron eigenstates yields the energy of interaction of the second group of charges with the full charge density in the crystal. Since this sum counts the self-energy of the second group of charges twice, we may subtract one contribution of this self-energy to yield the following expression for the conduction-electron contribution to the crystalline energy per ion:

$$\frac{1}{N}\left[\sum_{\{v\}}E_v-\frac{\Omega}{16\pi}\sum_{\{\mathbf{q}\}}{}'\,|\mathbf{q}|^2|\langle\mathbf{q}|V^{SC}|0\rangle|^2 -\int d\mathbf{r}\int d\mathbf{r}'\frac{(n_0)^2}{|\mathbf{r}-\mathbf{r}'|}\right]. \tag{45}$$

The last term in this expression is the self-energy of a uniform charge distribution with density n_0 equal to the average conduction-electron density in the crystal. Harrison[2] and Pick and Blandin[3] have shown that the sum over the valence states shown above may be expressed to second order in the pseudopotential by a sum over the free-electron Fermi sphere of $E_{\mathbf{k}}$, where

$$E_{\mathbf{k}}\equiv k^2+\bar{V}_L+\langle\mathbf{k}|W|\mathbf{k}\rangle +\sum_{\{\mathbf{q}\}}{}'\frac{\langle\mathbf{k}|W|\mathbf{k}+\mathbf{q}\rangle\langle\mathbf{k}+\mathbf{q}|W|\mathbf{k}\rangle}{|\mathbf{k}|^2-|\mathbf{k}+\mathbf{q}|^2}. \tag{46}$$

Since only the last two terms in Eq. (46) will vary when the ions are rearranged at constant volume, the conduction-electron contribution to the structure-dependent crystalline energy can be written as

$$E_{\mathrm{sd}}=\frac{1}{N}\sum_{\{\mathbf{k}\}_F}\langle\mathbf{k}|W|\mathbf{k}\rangle+\frac{1}{N}\sum_{\{\mathbf{q}\}}{}'\left(\sum_{\{\mathbf{k}_F\}}\frac{\langle\mathbf{k}|W|\mathbf{k}+\mathbf{q}\rangle\langle\mathbf{k}+\mathbf{q}|W|\mathbf{k}\rangle}{|\mathbf{k}|^2-|\mathbf{k}+\mathbf{q}|^2}-\frac{\Omega|\mathbf{q}|^2}{16\pi}|\langle\mathbf{q}|V^{SC}|0\rangle|^2\right). \quad (47)$$

Substituting for the matrix elements of W and V^{SC} from Eqs. (43) and (44) yields

$$E_{\mathrm{sd}}=\frac{1}{N}\sum_{\{\mathbf{k}\}_F}\langle\mathbf{k}|\bar{w}|\mathbf{k}\rangle+\sum_{\{\mathbf{q}\}}{}'\left[|S(\mathbf{q})|^2E_{11}(\mathbf{q})+|F(\mathbf{q})|^2E_{22}(\mathbf{q})\right]. \quad (48)$$

Here, the energy–wave-number characteristics are defined by

$$E_{ij}(\mathbf{q})\equiv\frac{1}{N}\left(\sum_{\{\mathbf{k}\}_F}\frac{\langle\mathbf{k}|w_i|\mathbf{k}+\mathbf{q}\rangle\langle\mathbf{k}+\mathbf{q}|w_j|\mathbf{k}\rangle}{|\mathbf{k}|^2-|\mathbf{k}+\mathbf{q}|^2}-\frac{\Omega|\mathbf{q}|^2}{16\pi}\langle 0|v_i|\mathbf{q}\rangle\langle\mathbf{q}|v_j|0\rangle\right), \quad (49)$$

where $w_1=\bar{w}$, $w_2=\Delta w$, $v_1=\bar{v}^{SC}$, and $v_2=\Delta v^{SC}$. The separability of the matrix elements of W and V^{SC} has resulted in the appearance of only the absolute magnitudes of $S(\mathbf{q})$ and $F(\mathbf{q})$ in Eq. (48). If the system is held at constant volume during the rearrangements of the ions and the $f_c(\mathbf{r})$ are restricted to be invariant during such rearrangements, then E_{sd} will vary only through $|S(\mathbf{q})|^2$ and $|F(\mathbf{q})|^2$. $|S(\mathbf{q})|^2$ is independent of the arrangement of the ions on the ionic sites and is accordingly invariant during the ordering process. $|F(\mathbf{q})|^2$ is discussed in the Appendix and shown to be a Fourier transform of a two-particle correlation function. Therefore, under these conditions, the variations in E_{sd} during the ordering process depend upon the position of the ions only through two-particle correlations.

In deriving an expression for the effective pairwise interaction, a form of E_{sd} which depends upon the arrangement of ions for a given atomic volume only through $S(\mathbf{q})$ and $F(\mathbf{q})$ must be used. Therefore, $f_c(\mathbf{r})$ is restricted, in this instance, to being independent of the arrangement of ions, so that the first term in Eq. (47) can be dropped. Substitution of Eqs. (43) and (44) into the remainder of Eq. (47), replacement of $S(\mathbf{q})$ and $F(\mathbf{q})$ by the sums over real space which they represent before taking their products, and interchanging the sums over real and reciprocal space yields

$$\frac{1}{2N}\sum_{\{\mathbf{R}\}}\sum_{\{\mathbf{R}'\}}\frac{2}{N}\sum_{\{\mathbf{q}\}}{}'e^{i\mathbf{q}\cdot(\mathbf{R}-\mathbf{R}')}\{E_{11}(\mathbf{q})+[\sigma(\mathbf{R}')-\langle\sigma\rangle_R]E_{12}(\mathbf{q})+[\sigma(\mathbf{R})-\langle\sigma\rangle_R]E_{21}(\mathbf{q})+[\sigma(\mathbf{R})-\langle\sigma\rangle_R][\sigma(\mathbf{R}')-\langle\sigma\rangle_R]E_{22}(\mathbf{q})\}. \quad (50)$$

This may be compared with the expression for the energy of the array of point charges, Z_i,

$$\frac{1}{2N}\sum_{\{\mathbf{R}\}\neq\{\mathbf{R}'\}}\sum\frac{1}{2|\mathbf{R}-\mathbf{R}'|}\{[(1+\sigma(\mathbf{R}))Z_A+(1-\sigma(\mathbf{R}))Z_B]\times[(1+\sigma(\mathbf{R}'))Z_A+(1-\sigma(\mathbf{R}'))Z_B]\}. \quad (51)$$

In Eq. (51), the interaction between an A ion at $\mathbf{R}$ and an A ion at $\mathbf{R}'$, for instance, can be obtained from the corresponding term in the double sum by setting $\sigma(\mathbf{R})=\sigma(\mathbf{R}')=1$. The effective pairwise interactions which follow are deduced by extending this approach to the electron contribution to the energy. Here, $V_{ij}(R)$ is the interaction between an ion of type i and one of type j separated by a distance R:

$$V_{AA}(R)=\frac{2Z_A^2}{R}+\frac{2}{N}\sum_{\{\mathbf{q}\}}{}'e^{i\mathbf{q}\cdot\mathbf{R}}\{E_{11}(\mathbf{q})+(1-\langle\sigma\rangle_R)[E_{12}(\mathbf{q})+E_{21}(\mathbf{q})]+[1-\langle\sigma\rangle_R]^2E_{22}(\mathbf{q})\}, \quad (52)$$

$$V_{BB}(R)=\frac{2Z_B^2}{R}+\frac{2}{N}\sum_{\{\mathbf{q}\}}{}'e^{i\mathbf{q}\cdot\mathbf{R}}\{E_{11}(\mathbf{q})-(1+\langle\sigma\rangle_R)[E_{12}(\mathbf{q})+E_{21}(\mathbf{q})]+(1+\langle\sigma\rangle_R)^2E_{22}(\mathbf{q})\}, \quad (53)$$

and

$$V_{AB}(R)=\frac{2Z_AZ_B}{R}+\frac{2}{N}\sum_{\{\mathbf{q}\}}{}'e^{i\mathbf{q}\cdot\mathbf{R}}\{E_{11}(\mathbf{q})+E_{12}(\mathbf{q})-E_{21}(\mathbf{q})-\langle\sigma\rangle_R[E_{12}(\mathbf{q})+E_{21}(\mathbf{q})]-(1-\langle\sigma\rangle_R{}^2)E_{22}(\mathbf{q})\}. \quad (54)$$

It must be emphasized that these forms arose as a consequence of using a second-order perturbation theory expression for the structure-dependent conduction-electron energy. Further, it was necessary to restrict $f_c(\mathbf{r})$ to being invariant during rearrangements of the ions at constant volume.

III. APPLICATION TO LiMg

The conduction-electron contributions to the ordering energy and to the effective pairwise interactions are evaluated below for stoichiometric LiMg. The selection of LiMg for these computations is motivated largely by our expectation that the approximations which have been introduced in this treatment are particularly applicable to this alloy of simple metals. While LiMg has not been found in a fully ordered state, Herbstein and Averbach[10] have measured a degree of short-range order in samples quenched from 200°C. Their experimental results suggest that LiMg would exhibit long-range order at low temperatures if the ions were sufficiently mobile at these temperatures that the alloy could readily reach equilibrium. The numerical values which are obtained here for this system should be consistent with these observations.

The choice of an optimal set of $f_c(\mathbf{r})$, which determine the pseudopotential, must not be taken lightly even though the work of Austin, Heine, and Sham[9] proves that the exact conduction-electron eigenvalues of a pseudopotential of the form of Eqs. (7) and (8) are independent of the $f_c(\mathbf{r})$. In this treatment, the final expressions for E_{sd} and for the effective pairwise interactions are the result of second-order perturbation theory and are therefore dependent upon the $f_c(\mathbf{r})$. Accordingly, the optimal set of $f_c(\mathbf{r})$ in this context will minimize the contribution of higher-order terms to E_{sd}. Pending the presentation of a detailed examination of the optimization procedure in a paper to be published shortly, the pseudopotential to be used here is given without a discussion of its selection. For use in a perturbation theory expansion of the properties of the conduction-electron eigenstate which has the plane wave $\mathbf{k}$ as a zeroth-order wave function, this pseudopotential may be expressed as

$$W=V^I+V^{SC}+\sum_c |c\rangle(k^2+\bar{V}_L+\langle\mathbf{k}|W|\mathbf{k}\rangle-E_c)\langle c|\,, \qquad (55)$$

where E_c is the eigenvalue of a crystalline core state. This pseudopotential is in the form discussed by Austin, Heine, and Sham[9] although Eq. (55) is $\mathbf{k}$-dependent. The Phillips and Kleinman pseudopotential,[11,12] which was derived from the OPW method, may be obtained from Eq. (55) by the substitution of the exact energy of the eigenstate for the first-order expression for that energy, $(k^2+\bar{V}_L+\langle\mathbf{k}|W|\mathbf{k}\rangle)$, which occurs in the sum over the core states. If the matrix elements of the crystalline core projection operator may be treated as first-order expressions in the pseudopotential, as has been assumed, then the Phillips and Kleinman pseudopotential will yield the same E_{sd} as Eq. (55) to second order in the pseudopotential. Taking the expectation value of Eq. (55) in the plane wave $\mathbf{k}$ leads to a self-consistent expression for the diagonal matrix elements of W,

$$\langle\mathbf{k}|W|\mathbf{k}\rangle = \frac{\langle\mathbf{k}|V^I+V^{SC}|\mathbf{k}\rangle+\sum_c |\langle\mathbf{k}|c\rangle|^2(k^2+\bar{V}_L-E_c)}{1-\sum_c |\langle\mathbf{k}|c\rangle|^2}. \qquad (56)$$

Expressions for the wave functions of the core electrons and for the $\bar{V}_L-E_c$ are needed for the evaluation of the matrix elements of the pseudopotential. Clementi's[13] analytic neutral atom Hartree-Fock Li and Mg eigenfunctions are used for the core wave functions. The procedure customarily employed to estimate the $\bar{V}_L-E_c$ in a single-element metallic crystal treats the ionic Hartree-Fock potential of the core as a first approximation to the crystalline potential seen by the core electron. The ionic Hartree-Fock eigenvalues are corrected by approximating the influence of an appropriate superposed periodic array of $N-1$ ions and a uniform distribution of the conduction electrons necessary for maintaining the charge neutrality of the crystal. Since the screening of the ions by the conduction electrons is neglected in this model, the interchange of a neighboring Li ion with a Mg ion would change the attractive potential of the ions dramatically without a compensating change in the repulsive electron potential to which a core electron is subject. Hence, the change in the core eigenvalues with ordering is vastly overestimated. Accordingly, we have used a neutral atom model for the calculation of the $\bar{V}_L-E_c$.

Considering a neutral atom of type A at the origin, a crystal is constructed by bringing neutral atoms of types A and B from infinity and placing them on the appropriate lattice sites. The atomic charge distributions are considered as fixed relative to their respective nuclei in this model. For stoichiometric LiMg in a body-centered cubic structure with a lattice constant of 3.5 Å, the added charge density at the origin calculated using Clementi's functions is no more than roughly 0.1% of the valence-electron charge already present. Therefore we will neglect effects related to this charge density at the origin, such as the associated exchange potential. Accordingly, $\bar{V}_L-E_c$ may be estimated for this system from the Hartree potential at the origin due to an array of lithium and magnesium neutral atoms. The electric field outside of a spherically symmetric charge distribution with a net charge Z is identical to that of a point charge of magnitude Z at the center of the distribution. Therefore, that portion of the neutral atom charge which lies within a sphere of radius equal to the nearest-neighbor distance will be treated as a point charge at the nucleus. For this system, the effective charges associated in this manner with the nuclei are 0.130 for lithium and 0.105 for magnesium. If the charge outside the sphere is treated as being uniformly distributed throughout the crystal, the correction to the

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atomic core eigenvalues may be estimated by the customary procedure.[8] In this model, the difference between $\bar{V}_L - E_c$ and the atomic eigenvalues would be roughly 0.13 Ry, which may be compared with a lithium $1S$ eigenvalue of -4.96 Ry and a magnesium $2P$ eigenvalue of -4.56 Ry.[13] The estimate of the corrections in the ordered and disordered states of the alloy would differ by roughly 0.008 Ry. Further, these corrections appear in the pseudopotential only when multiplied by the matrix elements of the core projection operator P, a first-order quantity. Due to their small magnitudes, we have neglected these corrections and used the neutral-atom Hartree-Fock eigenvalues of Clementi[13] to approximate $\bar{V}_L - E_c$ in stoichiometric LiMg.

The nonlocal ionic pseudopotential is readily computed from Eq. (20). However, the singularity caused by the vanishing of the denominators in Eqs. (33) and (34) must be treated with care in a numerical computation of the matrix elements of the screening potential. In this calculation, large negative and positive contributions from the singularity were paired off in direct analogy with the usual definitions of the principal part of an integral. The same procedure was used in computing the energy–wave-number characteristics as defined by Eq. (49). As we have neglected the change in $\bar{V}_L - E_c$, and hence in $f_c(\mathbf{r})$, during the ordering process, only $E_{22}(\mathbf{q})$ will contribute to the estimate of the conduction-electron contribution to the ordering energy. This function, multiplied by q^2, is plotted in Fig. 1. As discussed in the Appendix, $|F(\mathbf{q})|^2$ is nonvanishing only for certain discrete reciprocal-space vectors in the ordered state of the alloy. The magnitudes of these vectors are indicated in Fig. 1 by the short vertical bars. The number below each bar indicates the number of reciprocal-space vectors of that magnitude for which $|F(\mathbf{q})|^2$ is nonvanishing. The contribution of $E_{22}(\mathbf{q})$ to the energy of the ordered state is proportional to the sum of the values of E_{22} at each bar multiplied by that number. In the completely disordered state, $|F(\mathbf{q})|^2$ is a constant everywhere except for $\mathbf{q}$ a member of $\{\mathbf{K}\}$, where it vanishes. Thus the contribution of E_{22} to the disordered state is proportional to an integral of $q^2E_{22}(\mathbf{q})$ over all values of q. Accordingly, the conduction-electron contribution to the ordering energy is -0.0715 Ry per ion. The point-ion contribution to the ordering energy is the energy of a cesium chloride lattice of ± 0.5 charges, or 0.0768 Ry per ion. Therefore, we estimate that the internal energy of the ordered state is lower than that of the disordered state by 5.3 mRy per ion.

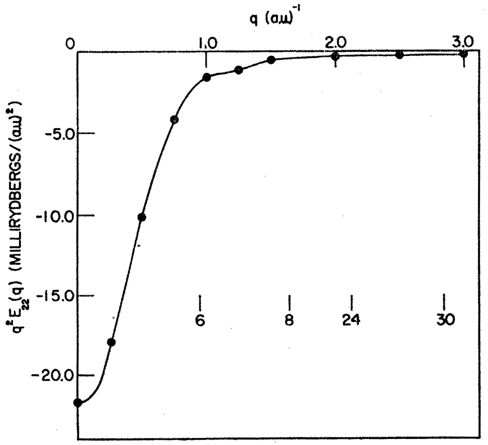

FIG. 1. The product of q^2 and the energy–wave-number characteristic $E_{22}(\mathbf{q})$ is plotted as a function of q, the distance from the origin in reciprocal space, for stoichiometric LiMg. The vertical bars and associated numbers indicate the positions and numbers of significant reciprocal-lattice vectors.

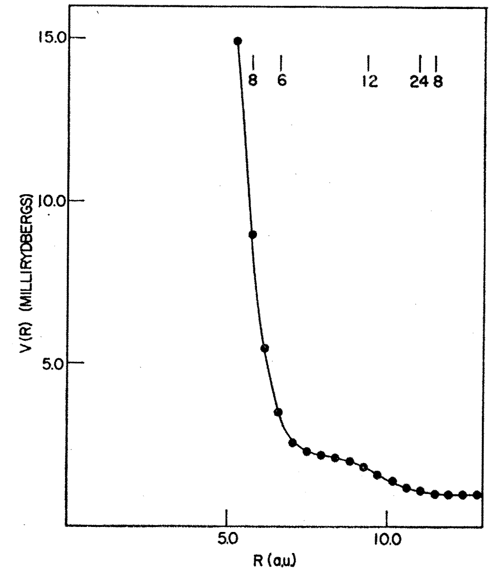

FIG. 2. The interaction $V \equiv V_{AA} + V_{BB} - 2V_{AB}$ is plotted as a function of R, the interionic separation, for stoichiometric LiMg. The vertical bars and associated numbers indicate the separations and numbers of the first five sets of near neighbors.

The effective pairwise interactions have been computed according to Eqs. (52)–(54). The effect of these interactions on the ordering process can be fully described in terms of $V \equiv V_{AA} + V_{BB} - 2V_{AB}$, which has been plotted as a function of ionic separation in Fig. 2. The short vertical bars and associated numbers indicate the positions and numbers of neighbors at each near-neighbor distance. In the ordered state of the alloy, the closest set of neighbors is unlike, the next two sets are like, the fourth is unlike, and the fifth is like the ion at the origin. These five sets of neighbors yield an ordering energy of 6.0 mRy per ion. However, since V is still quite large for more distant neighbors, the agreement between this estimate and the prior one, which included the contributions of all sets of neighbors, should be considered as largely coincidental.

Perhaps the most significant result of this numerical calculation is quite apparent in Fig. 2. If V is expressed approximately as a sum of an exponential term and a sinusoidal term, the former dominates throughout the region of this calculation.

As noted at the beginning of this section, the absence of an empirical estimate of the critical temperature of LiMg precludes a direct test of the accuracy of the results of this treatment of the alloy problem. However, the numerical value which has been obtained for the ordering energy should be consistent with the work of Herbstein and Averbach.[10] Any comparison between an empirical critical temperature, denoted by T_c, and a theoretical ordering energy, denoted by E, requires a statistical mechanical relation between these two quantities. Considering an Ising model with nearest-neighbor interactions only, Baker[14] has calculated a value of 1.587 for kT_c/E for a body-centered cubic system, where k is the Boltzmann constant. According to this relation, an ordering energy of 5.3 mRy corresponds to $T_c=1321$°K, which is much higher than would be expected from empirical observations. While Baker's work appears to demonstrate that the results of this treatment are inconsistent with experiment, the applicability of the nearest-neighbor Ising model to the LiMg system is questionable in light of the long-range nature of V, as obtained in this treatment. Chang[15] extended the second approximation of Bethe[16] by considering the interaction between both first and second nearest neighbors, denoted by V_1 and V_2, respectively, for values of V_2/V_1 between 0 and 0.25. For stoichiometric LiMg, our calculations indicate that $V_2/V_1=0.394$ and that the second and third nearest neighbors contribute roughly equal amounts to the ordering energy. If we approximate the effect of the third nearest neighbors by increasing V_2/V_1 to 0.794, Chang's results may be extrapolated to yield a decrease in kT_c/E by 58 to 67% of its value for $V_2/V_1=0$. Since $V_2/V_1=0.794$ is well into the region where Chang's calculations suggest that kT_c/E is very sensitive to the value of that ratio and we have extrapolated beyond the region of Chang's actual computation, the decrease in kT_c/E should be regarded as merely an indication of the nature of the dependence of that quantity on V_2/V_1. For example, if we were to assume that kT_c/E were 0.60, then an ordering energy of 5.3 mRy would correspond to $T_c=500$°K. This critical temperature is certainly consistent with the observation by Herbstein and Averbach that samples of stoichiometric LiMg which were quenched from 470°K exhibit a degree of short-range order.

While thermodynamic measurements do not, at present, yield a critical test of this theory, the treatment of Clapp and Moss[17] appears to provide a direct means of estimating V, apart from a constant multiplier. Their procedure yields the values of V at near-neighbor separations relative to the value at the nearest-neighbor separation from the diffuse x-ray scattering at temperatures considerably above T_c. This method is ideally suited for determining the shape of the interaction in the LiMg system, for which equilibrium may be anticipated at such temperatures, and thereby testing the predictions of this formalism.

APPENDIX: EVALUATION OF $|F(\mathbf{q})|^2$

The expression for the structure-dependent conduction-electron energy presented in Eq. (48) depends upon the positions of the ions during rearrangements at constant volume through the $|S(\mathbf{q})|^2$ and $|F(\mathbf{q})|^2$. Equation (18) may be used to write $|F(\mathbf{q})|^2$ as

$$F(\mathbf{q})F(-\mathbf{q})=\sum_{\{\mathbf{R}\}}\sum_{\{\mathbf{R}'\}}[\sigma(\mathbf{R})-\langle\sigma\rangle_R][\sigma(\mathbf{R}')-\langle\sigma\rangle_R]\times\frac{e^{-i\mathbf{q}\cdot\mathbf{R}}}{N}\frac{e^{+i\mathbf{q}\cdot\mathbf{R}'}}{N}. \quad (57)$$

The substitution of $\mathbf{R}'=\mathbf{R}+\mathbf{R}''$ into Eq. (57) yields

$$|F(\mathbf{q})|^2=\sum_{\{\mathbf{R}''\}}\langle\sigma(0)\sigma(\mathbf{R}'')\rangle_R\frac{e^{i\mathbf{q}\cdot\mathbf{R}''}}{N}, \quad (58)$$

where

$$\langle\sigma(0)\sigma(\mathbf{R}'')\rangle_R\equiv\sum_{\{\mathbf{R}\}}\frac{[\sigma(\mathbf{R})-\langle\sigma\rangle_R][\sigma(\mathbf{R}+\mathbf{R}'')-\langle\sigma\rangle_R]}{N}. \quad (59)$$

Since $\sigma(\mathbf{R})$ has been defined such that it has a value of $+1$ if $\mathbf{R}$ contains an A ion and -1 if $\mathbf{R}$ contains a B ion, Eq. (59) defines a two-particle correlation function. Accordingly, an expression for the conduction-electron energy which is accurate to second order in the pseudopotential depends upon the arrangement of ions during the ordering process only through a two-particle correlation function, apart from an optional dependence through $f_c(\mathbf{r})$.

$|F(\mathbf{q})|^2$ may be evaluated in terms of the Cowley order parameters.[18] The conditional probabilities $p_A(\mathbf{R})$ and $p_B(\mathbf{R})$ are the probabilities of finding an A ion located at $\mathbf{R}$ if the origin contains an A or a B ion, respectively. The Cowley order parameters, denoted by $\alpha(\mathbf{R})$, are defined by

$$p_B(\mathbf{R})=x-x\alpha(\mathbf{R}), \quad (60)$$

or, equivalently, by

$$p_A(\mathbf{R})=x+(1-x)\alpha(\mathbf{R}), \quad (61)$$

where x is the fraction of ions in the alloy which are of type A. These parameters have the properties that $\alpha(0)=1$ and that the sum of $\alpha(\mathbf{R})$ over all values of $\{\mathbf{R}\}$ vanishes. In analogy with Cowley's expression for the intensity of a diffracted x-ray beam,[19] the average

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defined by Eq. (59) is related to $\alpha(\mathbf{R})$ by

$$\langle\sigma(0)\sigma(\mathbf{R}')\rangle_R=4x(1-x)\alpha(\mathbf{R}')\,. \qquad (62)$$

Therefore, $|F(\mathbf{q})|^2$ may be expressed in terms of the Cowley order parameters as

$$|F(\mathbf{q})|^2=4x(1-x)\sum_{\{\mathbf{R}\}}\frac{\alpha(\mathbf{R})e^{i\mathbf{q}\cdot\mathbf{R}}}{N}\,. \qquad (63)$$

In a completely disordered alloy, $\alpha(\mathbf{R})$ must be a constant for all $\mathbf{R}\neq0$. The two properties of $\alpha(\mathbf{R})$ mentioned above imply that $\alpha(\mathbf{R})$ must equal $-1/(N-1)$ for all $\mathbf{R}\neq0$. Therefore, in the disordered alloy, $|F(\mathbf{q})|^2$ is given for a Bravais lattice by

$$|F(\mathbf{q})|^2=\frac{4x(1-x)}{N-1}[1-\Delta(\mathbf{q},\mathbf{K})]\,. \qquad (64)$$

The case of an ordered crystal is not as easily discussed since the exact form of $|F(\mathbf{q})|^2$ depends upon the particular structure involved. In the instance of a 50-50 alloy which orders in the cesium chloride structure, the lattice of ionic sites is body-centered cubic. In the ordered state, we may consider that A ions occupy all of the body centers and B ions occupy all of the corner sites. Accordingly, $\alpha(\mathbf{R})=1$ for all members of $\{\mathbf{R}\}$ which correspond to the set of repeating vectors for the ordered state, denoted by $\{\mathbf{R}_s\}$. For all other sites in $\{\mathbf{R}\}$, $\alpha(\mathbf{R})$ is equal to $1-(1/x)$, or -1 in this case. Therefore, $|F(\mathbf{q})|^2$ is given by

$$|F(\mathbf{q})|^2=4x(1-x)\left[-\sum_{\{\mathbf{R}\}}\frac{e^{i\mathbf{q}\cdot\mathbf{R}}}{N}+\sum_{\{\mathbf{R}_s\}}\frac{e^{i\mathbf{q}\cdot\mathbf{R}_s}}{\frac{1}{2}N}\right]. \qquad (65)$$

If $\mathbf{q}$ is any member of the set $\{\mathbf{K}\}$, then both sums in this expression are unity and $|F(\mathbf{q})|^2$ vanishes. This is in agreement with the previously noted property that $F(\mathbf{K})=0$. If $\mathbf{q}$ is not a member of $\{\mathbf{K}_s\}$, the set of reciprocal-lattice vectors corresponding to $\{\mathbf{R}_s\}$, then both sums are zero and $|F(\mathbf{q})|^2$ vanishes. If $\mathbf{q}$ is a member of $\{\mathbf{K}_a\}$, which consists of those members of $\{\mathbf{K}_s\}$ which are not members of $\{\mathbf{K}\}$, then the first sum is zero and the second is unity. Accordingly, for the ordered case, we may write $|F(\mathbf{q})|^2$ as

$$|F(\mathbf{q})|^2=4x(1-x)\Delta(\mathbf{q},\mathbf{K}_a)\,. \qquad (66)$$

In general, $|F(\mathbf{q})|^2$ is zero in the ordered state of any alloy except for $\mathbf{q}$ equal to appropriate reciprocal-lattice vectors.

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Electronic Structure of One-Dimensional Binary Alloys*

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The electronic structure of one-dimensional binary alloys is studied in terms of exact mathematical expressions. It is shown by counter examples that the Saxon-Hutner theorem and its converse do not necessarily hold for all potentials. The exact phase transfer theory is used. The present approach has the advantage that it can examine with the same ease both the Saxon-Hutner theorem and its converse. Various sufficient conditions of validity are found. The physical content of these conditions for potentials that are localized and symmetric is analyzed by means of the one-dimensional scattering phase shifts of the individual constituent potentials. As an example, it is shown that both the Saxon-Hutner theorem and its converse are valid if the phase shifts of the two localized symmetric potentials forming the binary alloy are solutions belonging to a certain class T, in which the even and odd phase shifts of type-A and type-B symmetric potentials indicated by α_+, β_+, and α_-, β_-, respectively, satisfy the condition $[\sin(\alpha_++\alpha_-)/\sin(\alpha_+-\alpha_-)]=[\sin(\beta_++\beta_-)/\sin(\beta_+-\beta_-)]=f$, where f is a constant. The analysis can be trivially extended to the study of alloys composed of more than two elements.

INTRODUCTION

In 1949 Saxon and Hutner[1] put forth an interesting conjecture concerning the forbidden energy levels of a one-dimensional binary alloy. In a form modified for our purpose here it states that a level, which is forbidden in the infinite one-dimensional lattice formed of pure type-A potentials and in that formed of pure type-B potentials, is also forbidden in any arbitrary substitutional alloy and A and B. We shall call this the Saxon-Hutner theorem. The original conjecture by Saxon-Hutner refers only to δ potentials of the Kronig-Penney type situated at the centers of equal cells, and has been proved by Luttinger[2] and Dworin[3] and demonstrated by numerical computations of Agacy and Borland.[4] Since then, many have questioned whether this conjec-

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