PHYSICAL REVIEW B VOLUME 26, NUMBER 8 15 OCTOBER 1982

Self-consistent harmonic approximation for atomic static displacements in alloys

Genrich L. Krasko*
Institut für Theoretische Physik, Universität Tübingen, D-7400 Tübingen, West Germany
(Received 1 February 1982)

A self-consistent harmonic approximation for the static displacements of host atoms in a crystal lattice due to interstitial impurities is introduced. It is shown that at a certain concentration of the impurity the loss of stability arises; for higher concentrations there are no real solutions of the equilibrium equation for displacements as well as for the phonon frequencies. A criterion for the mean-square displacements, analogous to Lindemann's criterion in the theory of melting, may be introduced. The phenomenological rule that the maximal concentration of hydrogen atoms in a transition-metal system corresponds to an average *d*-electron concentration, DEC$\simeq$ 5, is explained using the new Lindemann's criterion.

I. INTRODUCTION

Since the pioneering works[1,2] appeared, considerable success has been achieved in the microscopic theory of elastic interaction in interstitial alloys and compounds, and particularly in metal-hydrogen systems.

Among the most important phenomena originating from elastic interaction which the new approach has managed to investigate were phase transitions both of gas-liquid[2] and order-disorder[3] type. The elastic interaction may also lead to the loss of stability of a crystal lattice. The concentration of impurity corresponding to this point at a given temperature is the maximally possible one for a given system. It is very important from a practical point of view to be able to find the conditions allowing for the maximal concentration of impurity in a still stable crystal.

In order to be able to consider a criterion of elastic stability of an interstitial solid solution we will develop an approach that may be called the "self-consistent harmonic approximation" (SCHA) for atomic static displacements. The latter is a counterpart of the approach developed in lattice dynamics, the self-consistent phonon approximation,[4] which has been successfully used in the thermodynamics of rare-gas crystals[5] and melting.[6]

In 1975, in a Letter,[7] we used the SCHA without proof to explain the well-known phenomenological criterion of solubility in substitutional solid solutions suggested by Hume-Rothery[8] almost 50 years ago. In the present work we are going to justify this approach and show how it may predict the elastic instability in an interstitial solid solution, and, particularly, a metal-hydrogen system.

II. STATIC DISPLACEMENTS IN INTERSTITIAL SOLID SOLUTIONS AND THE HARMONIC HAMILTONIAN

Let us consider a crystal with the host atoms in the crystal lattice sites and the impurity atoms occupying some interstitial positions. If we suppose that the atoms interact via pairwise potentials, the Hamiltonian reads

$$H=\frac{1}{2}\sum_{\vec{\mathscr{R}},\vec{\mathscr{R}}'}{}' U(\vec{\mathscr{R}}-\vec{\mathscr{R}}')+\sum_{\vec{\mathscr{R}},\vec{\mathscr{R}}'} V^p(\vec{\mathscr{R}}-\vec{\mathscr{R}}')C^p_{\vec{\mathscr{R}}'} + \frac{1}{2}\sum_{\substack{\vec{\mathscr{R}}\,\vec{\mathscr{R}}'\\(\vec{\mathscr{R}},p\neq\vec{\mathscr{R}}',p')}} (\vec{\mathscr{R}}-\vec{\mathscr{R}}')C^p_{\vec{\mathscr{R}}}C^{p'}_{\vec{\mathscr{R}}'}\ . \tag{1}$$

Here the first term is the interaction energy of the host atoms; the second one is the sum of interactions of a host atom at lattice site $\vec{\mathscr{R}}$ with an interstitial atom in the pth interstitial position of the $\vec{\mathscr{R}}'$th unit cell. (For simplicity we are considering a Bravais lattice.) The third term is a direct interaction of the impurity atoms. The potential $W^{pp'}(\vec{\mathscr{R}}-\vec{\mathscr{R}}')$ is of short range and, since the concentration of interstitial atoms is usually low, it is often neglected.[2] In Eq. (1) $C^p_{\vec{\mathscr{R}}}$ is a random quantity equal to 1 if there is an atom in the pth interstitial position of the $\vec{\mathscr{R}}$th unit cell, and 0 otherwise. The repeating indices p,p' mean summation;

$p,p'=1,2,\dots,\nu$, where ν is the number of the interstitial positions in each unit cell that may be occupied.

The set $\{\vec{\mathscr{R}}\}$ does not form a perfect crystal lattice because of static displacements due to interstitial atoms. In fact,

$$\vec{\mathscr{R}}=\vec{\mathrm{R}}+\vec{\mathrm{u}}_{\vec{\mathrm{R}}}\ .$$

Here $\vec{\mathrm{u}}_{\vec{\mathrm{R}}}$ is the nonuniform part of the displacement. The uniform displacement allowing for the "concentrational expansion" of the lattice is included into the first term, so that $\{\vec{\mathrm{R}}\}$ means the regular "average" lattice after the concentrational expansion. X-ray diffraction experiments just give the values of the lattice parameter of $\{\vec{\mathrm{R}}\}$ that depends on $\bar{c}$, the average concentration of the impurity atoms. Obviously, $\sum_{\vec{\mathrm{R}}}\vec{\mathrm{u}}_{\vec{\mathrm{R}}}=0$.

We impose periodic boundary conditions and write the Hamiltonian, Eq. (1), as a Fourier series in the volume Ω ($\Omega=\Omega_0 N$, where N is the total number of unit cells within the volume and Ω_0 is the volume of the unit cell):

$$H=\frac{1}{2}\frac{1}{\Omega}\sum_{\vec{\mathrm{q}}}U_{\vec{\mathrm{q}}}\sum_{\vec{\mathrm{R}},\vec{\mathrm{R}}'}{}' e^{i\vec{\mathrm{q}}\cdot(\vec{\mathrm{R}}-\vec{\mathrm{R}}'+\vec{\mathrm{u}}_{\vec{\mathrm{R}}}-\vec{\mathrm{u}}_{\vec{\mathrm{R}}'})}+\frac{1}{\Omega}\sum_{\vec{\mathrm{q}}}V^{p}_{\vec{\mathrm{q}}}\sum_{\vec{\mathrm{R}},\vec{\mathrm{R}}'}e^{i\vec{\mathrm{q}}\cdot(\vec{\mathrm{R}}-\vec{\mathrm{R}}'+\vec{\mathrm{u}}_{\vec{\mathrm{R}}}-\vec{\mathrm{u}}_{\vec{\mathrm{R}}'})}C^{p}_{\vec{\mathrm{R}}'}$$
$$+\frac{1}{2}\frac{1}{\Omega}\sum_{\vec{\mathrm{q}}}W^{pp'}_{\vec{\mathrm{q}}}\sum_{\vec{\mathrm{R}},\vec{\mathrm{R}}'}e^{i\vec{\mathrm{q}}\cdot(\vec{\mathrm{R}}-\vec{\mathrm{R}}'+\vec{\mathrm{u}}_{\vec{\mathrm{R}}}-\vec{\mathrm{u}}_{\vec{\mathrm{R}}'})}C^{p}_{\vec{\mathrm{R}}}C^{p'}_{\vec{\mathrm{R}}'}\ , \tag{2}$$

where $U_{\vec{\mathrm{q}}}$, $V^{p}_{\vec{\mathrm{q}}}$, and $W^{pp'}_{\vec{\mathrm{q}}}$ are the Fourier transforms of the corresponding potentials in Eq. (1).

We now introduce a new random quantity corresponding to concentration fluctuations:

$$\Delta c^{p}_{\vec{\mathrm{R}}}=c^{p}_{\vec{\mathrm{R}}}-\frac{\bar{c}}{\nu}\ .$$

Obviously,

$$\frac{1}{N}\sum_{\vec{\mathrm{R}}}c^{p}_{\vec{\mathrm{R}}}=\frac{\bar{c}}{\nu},\quad \frac{1}{N}\sum_{\vec{\mathrm{R}}}\Delta c^{p}_{\vec{\mathrm{R}}}=0\ .$$

Then Eq. (2) may be rewritten

$$H=\frac{1}{2}\frac{1}{\Omega}\sum_{\vec{\mathrm{q}}}\mathscr{U}_{\vec{\mathrm{q}}}\sum_{\vec{\mathrm{R}},\vec{\mathrm{R}}'}{}' e^{i\vec{\mathrm{q}}\cdot(\vec{\mathrm{R}}-\vec{\mathrm{R}}'+\vec{\mathrm{u}}_{\vec{\mathrm{R}}}-\vec{\mathrm{u}}_{\vec{\mathrm{R}}'})}+\frac{1}{\Omega}\sum_{\vec{\mathrm{q}}}\mathscr{V}^{p}_{\vec{\mathrm{q}}}\sum_{\vec{\mathrm{R}},\vec{\mathrm{R}}'}e^{i\vec{\mathrm{q}}\cdot(\vec{\mathrm{R}}-\vec{\mathrm{R}}'+\vec{\mathrm{u}}_{\vec{\mathrm{R}}}-\vec{\mathrm{u}}_{\vec{\mathrm{R}}'})}\Delta c^{p}_{\vec{\mathrm{R}}'}$$
$$+\frac{1}{2}\frac{1}{\Omega}\sum_{\vec{\mathrm{q}}}W^{pp'}_{\vec{\mathrm{q}}}\sum_{\vec{\mathrm{R}},\vec{\mathrm{R}}'}e^{i\vec{\mathrm{q}}\cdot(\vec{\mathrm{R}}-\vec{\mathrm{R}}'+\vec{\mathrm{u}}_{\vec{\mathrm{R}}}-\vec{\mathrm{u}}_{\vec{\mathrm{R}}'})}\Delta c^{p}_{\vec{\mathrm{R}}}\Delta c^{p}_{\vec{\mathrm{R}}'}\ , \tag{3}$$

where

$$\mathscr{U}_{\vec{\mathrm{q}}}=U_{\vec{\mathrm{q}}}+\frac{2\bar{c}}{\nu}\sum_{p=1}^{\nu}V^{p}_{\vec{\mathrm{q}}}+\frac{\bar{c}^{2}}{\nu^{2}}\sum_{p,p'=1}^{\nu}W^{pp'}_{\vec{\mathrm{q}}}\ , \tag{4a}$$

$$\mathscr{V}^{p}_{\vec{\mathrm{q}}}=V^{p}_{\vec{\mathrm{q}}}+\frac{\bar{c}}{\nu}\sum_{p'=1}^{\nu}W^{pp'}_{\vec{\mathrm{q}}}\ . \tag{4b}$$

Now we are going to make use of a harmonic approximation. In our case this will mean keeping the terms up to second order not only in the displacements $\vec{\mathrm{u}}_{\vec{\mathrm{R}}}$ but also in the concentration fluctuations $\Delta c^{p}_{\vec{\mathrm{R}}}$. Then the total Hamiltonian is

$$H=H_h+O(\vec{\mathrm{u}}^{3},\Delta c^{3})\ ,$$

and the harmonic Hamiltonian reads

$$H_h=H_0+\Delta H_h\ ,$$

where

$$H_0=\frac{1}{2}\frac{1}{\Omega}\sum_{\vec{q}}\mathscr{U}_{\vec{q}}\sum_{\vec{R},\vec{R}'}e^{i\vec{q}\cdot(\vec{R}-\vec{R}')}\,, \tag{5a}$$

$$\begin{aligned}\Delta H_h=&-\frac{1}{2}\frac{1}{\Omega}\sum_{\vec{q}}\mathscr{U}_{\vec{q}}\sum_{\vec{R},\vec{R}'}e^{i\vec{q}\cdot(\vec{R}-\vec{R}')}\tfrac{1}{2}[\vec{q}\cdot(\vec{u}_{\vec{R}}-\vec{u}_{\vec{R}'})]^2\\&+\frac{1}{\Omega}\sum_{\vec{q}}\mathscr{V}^{p}_{\vec{q}}\sum_{\vec{R},\vec{R}'}e^{i\vec{q}\cdot(\vec{R}-\vec{R}')}i[\vec{q}\cdot(\vec{u}_{\vec{R}}-\vec{u}_{\vec{R}'})]\Delta c^{p}_{\vec{R}'}\\&+\frac{1}{2}\frac{1}{\Omega}\sum_{\vec{q}}W^{pp'}_{\vec{q}}\sum_{\vec{R},\vec{R}'}e^{i\vec{q}\cdot(\vec{R}-\vec{R}')}\Delta c^{p}_{\vec{R}}\,\Delta c^{p'}_{\vec{R}'}\,.\end{aligned} \tag{5b}$$

Equations (5a) and (5b) may be written in another form:

$$H_0=\tfrac{1}{2}\sum_{\vec{R},\vec{R}'}{}'\,\mathscr{U}(\vec{R}-\vec{R}')\,, \tag{6a}$$

$$\begin{aligned}\Delta H_h=&\tfrac{1}{2}\sum_{\vec{R},\vec{R}'}\mathscr{A}^{ij}(\vec{R}-\vec{R}')u^{i}_{\vec{R}}u^{j}_{\vec{R}'}\\&-\sum_{\vec{R},\vec{R}'}F^{i}_{p}(\vec{R}-\vec{R}')u^{i}_{\vec{R}}\,\Delta c^{p}_{\vec{R}'}\\&+\tfrac{1}{2}\sum_{\vec{R},\vec{R}'}W^{pp'}(\vec{R}-\vec{R}')\Delta c^{p}_{\vec{R}}\,\Delta c^{p'}_{\vec{R}}\ .\end{aligned} \tag{6b}$$

Here $\mathscr{U}(\vec{R}-\vec{R}')$ has the meaning of an effective interaction of the host atoms in the "average" lattice, allowing for the effects of an absolutely random distribution of the impurity atoms. The lattice-vibration spectrum of such a lattice would be defined by a dynamical matrix, which happens to be just identical to $\mathscr{A}^{ij}(\vec{R}-\vec{R}')$ of Eq. (6b) (although the displacements $u^{i}_{\vec{R}}$ here are not dynamic, the static ones are). Obviously,

$$\begin{aligned}\mathscr{A}^{ij}(\vec{R}\neq\vec{R}')&=\frac{1}{\Omega}\sum_{\vec{q}}q^iq^j\mathscr{U}_{\vec{q}}e^{i\vec{q}\cdot(\vec{R}-\vec{R}')}\,,\\ \mathscr{A}^{ij}(\vec{R}=\vec{R}')&=-\frac{1}{\Omega}\sum_{\vec{q}}q^iq^j\mathscr{U}_{\vec{q}}\sum_{R''}e^{i\vec{q}\cdot\vec{R}}\ .\end{aligned} \tag{7}$$

$F^{i}_{p}(\vec{R}-\vec{R}')$ has the meaning of a force acting between the host atom in lattice site $\vec{R}$ and the impurity atom in position p of the $\vec{R}'$th unit cell. (i,j) in Eqs. (6b) and (7) are Cartesian indices.

The harmonic Hamiltonian, Eqs. (6a) and (6b), depends on two random quantities $\{\vec{u}_{\vec{R}}\}$ and $\{\Delta c^{p}_{\vec{R}}\}$. However, they are not independent. At a fixed (arbitrary) distribution of the impurity atoms $\{\Delta c^{p}_{\vec{R}}\}$, the $\vec{u}_{\vec{R}}$'s may be found from the minimization requirement:

$$\frac{\delta H_h}{\delta\vec{u}_{\vec{R}}}=0\ .$$

The corresponding equation reads

$$\sum_{\vec{R}'}\mathscr{A}^{ij}(\vec{R}-\vec{R}')u^{j}_{\vec{R}'}-\sum_{\vec{R}'}F^{i}_{p}(\vec{R}-\vec{R}')\Delta c^{p}_{\vec{R}'}=0\ . \tag{8}$$

The eigenvalues of operator $\hat{A}$ are just vibration frequencies of the average lattice:

$$\mathscr{A}^{ij}(\vec{\kappa})e^{j}_{\sigma}(\vec{\kappa})=m\omega^2_{\sigma}(\vec{\kappa})e^{i}_{\sigma}(\vec{\kappa})\ . \tag{9}$$

Here $\omega_\sigma(\vec{\kappa})$ and $e^{i}_{\sigma}(\kappa)$ are the frequencies and polarization vectors corresponding to the σth branch of vibration (a Bravais lattice has only acoustic branches $\sigma=1,2,3$). $\mathscr{A}^{ij}(\vec{\kappa})$ is the Fourier transform of the dynamical matrix, Eq. (7),

$$\mathscr{A}^{ij}(\vec{\kappa})=\sum_{\vec{R}}\mathscr{A}^{ij}(\vec{\mathscr{R}})e^{i\vec{\kappa}\cdot\vec{R}} \tag{7'}$$

(vectors $\vec{\kappa}$ are defined within the Brillouin zone of the lattice $\{\vec{R}\}$), and m is the (effective) mass of vibrating ("average") host atoms.

Now, making use of the Green's-function tensor,

$$G^{ij}(\vec{\kappa})=\sum_{\sigma=1}^{3}\frac{e^{i}_{\sigma}(\vec{\kappa})e^{j}_{\sigma}(\vec{\kappa})}{m\omega^2_{\sigma}(\vec{\kappa})}\,,$$

one immediately obtains the solution to Eq. (8):

$$u^{i}(\vec{\kappa})=\sum_{\sigma=1}^{3}\frac{e^{i}_{\sigma}(\vec{\kappa})e^{j}_{\sigma}(\vec{\kappa})F^{j}_{p}(\vec{\kappa})\Delta c^{p}(\vec{\kappa})}{m\omega^2_{\sigma}(\vec{\kappa})}\,, \tag{10a}$$

where

$$u^{i}(\vec{\kappa})=\sum_{\vec{R}}u^{i}_{\vec{R}}e^{i\vec{\kappa}\cdot\vec{R}}\ , \tag{10b}$$

$$\Delta c^{p}(\vec{\kappa})=\sum_{\vec{R}}\Delta c^{p}_{\vec{R}}e^{i\vec{\kappa}\cdot\vec{R}}\ . \tag{10c}$$

The method of solving Eq. (8) and the solution, Eq. (10a), were first suggested in Ref. 1 (see also Refs. 9 and 10). There, however, the dynamical matrix and ω^2 corresponded to the pure host lattice, while in our case the effects of homogeneous impurity distribution are also incorporated (by introducing the "average" lattice).

Now let us return to Eq. (8). Having substituted it in Eq. (6b) one obtains:

$$\Delta H_h = -\tfrac{1}{2} \sum_{\vec{R},\vec{R}'} \mathscr{A}^{ij}(\vec{R}-\vec{R}') u^i_{\vec{R}} u^j_{\vec{R}'} + \tfrac{1}{2} \sum_{\vec{R},\vec{R}'} W^{pp'}(\vec{R}-\vec{R}') \Delta c^p_{\vec{R}} \Delta c^{p'}_{\vec{R}'} , \tag{11}$$

where now $u^i_{\vec{R}}$ are the solutions of Eq. (8) and are defined via Eq. (10a).

At this stage we are going to drop the second term in Eq. (11), the direct interaction of impurity-atom fluctuations. Note that we do keep the impurity interaction for the uniform distribution of impurity atoms, which contributes to the interatomic interactions in the "average" lattice, Eqs. (4a) and (4b). Now

$$\Delta H_h = -\tfrac{1}{2} \sum_{\vec{R},\vec{R}'} \mathscr{A}^{ij}(\vec{R}-\vec{R}') u^i_{\vec{R}} u^j_{\vec{R}'} . \tag{11'}$$

We may now return to the expression of the type of Eqs. (5a) and (5b) and write

$$\begin{aligned} H_h &= H_0 + \Delta H_h \\ &= \frac{1}{2}\frac{1}{\Omega} \sum_{\vec{q}} \mathscr{U}_{\vec{q}} \sum_{\vec{R},\vec{R}'}{}' e^{i\vec{q}\cdot(\vec{R}-\vec{R}')} \\ &\quad \times \{1 + \tfrac{1}{2}[\vec{q}\cdot(\vec{u}_{\vec{R}} - \vec{u}_{\vec{R}'})]^2\} . \end{aligned} \tag{12}$$

Here again we point out that $\vec{u}_{\vec{R}}$ are random quantities which are defined via another set of random quantities $\Delta c^p_{\vec{R}}$ by Eqs. (10b) and (10c). From now on we will be working with the harmonic Hamiltonian, Eq. (12).

III. SELF-CONSISTENT HARMONIC APPROXIMATION

We are going to consider now a more general problem of calculating the partition function. Let the Hamiltonian consist of only potential energy, i.e., it corresponds to a static classical system:

$$H \equiv V . \tag{13}$$

Let there further exist an approximation H_h that allows an exact (or easy) solution. We will be referring to H_h as a "harmonic" Hamiltonian. Then Eq. (13) identically reads

$$H = H_h + v, \quad v = V - H_h . \tag{14}$$

We are going to consider a Gibbs ensemble with the partition function

$$Z = \mathrm{Tr}(e^{-\beta H}) , \tag{15}$$

where $\beta = 1/T$, T is the absolute temperature in energy units, and Tr( ) means the trace: summation (or integration) over all the microstates of the (classical) system.

With Eq. (14) one has

$$Z = e^{-\beta\langle v\rangle_0} Z_0 \langle e^{-\beta\Delta v}\rangle_0 , \tag{16a}$$

where

$$Z_0 = \mathrm{Tr}(e^{-\beta H_h}) , \tag{16b}$$

$$\langle\ \rangle_0 = \frac{1}{Z_0}\mathrm{Tr}(\cdots e^{-\beta H_h}) , \tag{16c}$$

and

$$\Delta v = v - \langle v\rangle_0 . \tag{16d}$$

The last factor in Eq. (16a), the average, is conveniently considered as a series in so-called "central moments," $\mu_n = \langle \Delta v^n\rangle_0$. Then

$$Z = Z_0 e^{-\beta\langle v\rangle_0} \left[1 + \sum_{n=2}^{\infty} \frac{(-\beta)^n}{n!}\mu_n \right] . \tag{17}$$

Now we are going to introduce a "fictitious" harmonic approximation,

$$\tilde{H}_h = \hat{\alpha} H_h , \tag{18}$$

where $\hat{\alpha}$ is a (nonrandom) operator, and we will try to find such an $\hat{\alpha}$ that the relative difference between the exact Z, Eq. (16a), and

$$Z_h = Z_0 e^{-\beta\langle\tilde{v}\rangle_0} \tag{19}$$

is minimal. To be precise, we require that

$$\frac{\delta}{\delta\hat{\alpha}} \left[1 - \frac{Z_h}{Z} \right]^2 = 0 . \tag{20a}$$

In Eq. (19) $\langle\ \rangle_0$ now means the average over the Gibbs ensemble with the Hamiltonian $\tilde{H}_h$, Eq. (18), and $\tilde{v} = V - \tilde{H}_h$.

Since Z does not depend on $\hat{\alpha}$, Eq. (20a) is equivalent to

$$\frac{\delta}{\delta\hat{\alpha}}(Z_0 e^{-\beta\langle\tilde{v}\rangle_0})=0\ . \tag{20b}$$

Making use of the definitions, Eqs. (16b)–(16d), the variational derivative, Eq. (20b), reads

$$\langle H_h\hat{\alpha}H_h\rangle_0-\langle H_h\rangle_0\langle\hat{\alpha}H_h\rangle_0 =\langle H_h V\rangle_0-\langle H_h\rangle_0\langle V\rangle_0 \tag{21a}$$

or

$$\langle H_h\tilde{v}\rangle_0=\langle H_h\rangle_0\langle\tilde{v}\rangle_0\ . \tag{21b}$$

The $\tilde{H}_h$ with $\hat{\alpha}$ satisfying Eqs. (21a) and (21b) will be referred to as the SCHA. One can easily see that condition (20b) is equivalent to the minimization, with respect to $\hat{\alpha}$, of Gibbs free energy,

$$\Phi=-\frac{1}{\beta}\ln(Z_0 e^{-\beta\langle\tilde{v}\rangle_0})\ .$$

Then the requirement that the solution corresponds to a minimum of Φ,

$$\frac{\delta^2\Phi}{\delta\hat{\alpha}^2}>0\ ,$$

reads

$$\beta^2(\langle H_h\rangle_0^2\langle\tilde{v}\rangle_0-2\langle H_h\rangle_0\langle H_h\tilde{v}\rangle_0+\langle H_h^2\tilde{v}\rangle_0)>0\ ,$$

and for $\hat{\alpha}$ satisfying Eq. (20b),

$$\beta^2(\langle H_h^2\tilde{v}\rangle_0-\langle H_h^2\rangle_0\langle\tilde{v}\rangle_0)>0\ .$$

The loss of stability $\delta^2\Phi/\delta\hat{\alpha}^2=0$ occurs for

$$\langle H_h^2\tilde{v}\rangle_0=\langle H_h^2\rangle_0\langle\tilde{v}\rangle_0\ .$$

Note also, that the Eqs. (21a) and (21b) hold if one requires a minimum of the second central moment μ_2 with respect to $\hat{\alpha}$.

Returning to Eqs. (21a) and (21b) we may now attempt to find the SCHA corresponding to H_h for static displacements, Eq. (12). Let the operator $\hat{\alpha}$ belong to quite a general class, such that

$$\hat{\alpha}H_h=\frac{1}{\Omega}\sum_{\vec{q}}\mathscr{U}_{\vec{q}}\sum_{\vec{R},\vec{R}'}\alpha_{\vec{q}}(\vec{R}-\vec{R}')e^{i\vec{q}\cdot(\vec{R}-\vec{R}')} \times\{1+\tfrac{1}{2}[\vec{q}\cdot(\vec{u}_{\vec{R}}-\vec{u}_{\vec{R}'})]^2\}\ , \tag{22}$$

where $\alpha_{\vec{q}}(\vec{R}-\vec{R}')$ is a function of q and $\vec{R}-\vec{R}'$.

In order to simplify the formula we will introduce the notations

$$\sum_{\vec{q}}\sum_{(1)}\{\ \}\equiv\frac{1}{2}\frac{1}{\Omega}\sum_{\vec{q}}\mathscr{U}_{\vec{q}}\sum_{\vec{R},\vec{R}'}{}' e^{i\vec{q}\cdot(\vec{R}-\vec{R}')}\{\ \}\ ,$$

$$\Delta\vec{u}_1=\vec{u}_{\vec{R}_1}-\vec{u}_{\vec{R}_1'},\quad \alpha_{\vec{q}}^{(1)}=\alpha_{\vec{q}}(\vec{R}-\vec{R}')\ .$$

Then

$$\tilde{H}_h\equiv\hat{\alpha}H_h=\sum_{\vec{q}}\sum_{(1)}\{\alpha_{\vec{q}}^{(1)}[1+\tfrac{1}{2}(\vec{q}\cdot\Delta\vec{u}_1)^2]\}\ ,$$

$$V\equiv H=\sum_{\vec{q}}\sum_{(1)}\{e^{i\vec{q}\cdot\Delta\vec{u}_1}\}\ . \tag{23}$$

Taking the variational derivative, Eq. (20b), with respect to $\alpha_{\vec{q}}(\vec{R}-\vec{R}')$, one obtains the equation

$$\sum_{\vec{q}'}\sum_{(2)}\{\alpha_{\vec{q}'}^{(2)}[\langle(\vec{q}\cdot\Delta\vec{u}_1)^2(\vec{q}'\cdot\vec{\Delta}u_2)^2\rangle_0-\langle(\vec{q}\cdot\Delta\vec{u}_1)^2\rangle_0\langle(\vec{q}'\cdot\Delta\vec{u}_2)^2\rangle_0] +2[\langle(\vec{q}\cdot\Delta\vec{u}_1)^2 e^{i\vec{q}'\cdot\Delta\vec{u}_2}\rangle_0-\langle(\vec{q}\cdot\Delta\vec{u}_1)^2\rangle_0\langle e^{i\vec{q}'\cdot\Delta\vec{u}_2}\rangle_0]\}=0\ . \tag{24}$$

In order to solve this equation for α one needs to calculate the averages.

If the distribution of displacements were Gaussian, the calculations could easily be performed. However, as was pointed out by Krivoglaz (see Sec. 24 of Ref. 10), it is not. In spite of the quadratic form of the Hamiltonian, Eq. (12), and the fact that the displacement of each host atom u_R is the superposition of a macroscopically great number of displacements due to individual impurity atoms $\Delta\vec{u}^p(\vec{R}-\vec{R}')$,

$$\vec{u}_{\vec{R}}=\sum_{\vec{R}'}\Delta\vec{u}^p(\vec{R}-\vec{R}')\Delta c_{\vec{R}'}^p\ ,$$

there may be significant deviations from the Gaussian behavior because of the prevalent role of nearest neighbors. From the mathematical point of view this finds its manifestation in that the random quantities $\Delta c^p(\vec{\kappa})$ on which each $\vec{u}_{\vec{R}}$ depends, Eqs. (10a) and (10b), do not run all the possible values (the latter would correspond to the Gaussian distribution of $\vec{u}_{\vec{R}}$). In fact, the number of impurity atoms is constant. Therefore,

$$\frac{1}{N}\sum_{\vec{R}}\sum_{p=1}^{\nu}c_{\vec{R}}^p=\frac{\bar{c}}{\nu}\ .$$

Further, since $(c_{\vec{R}}^p)^2\equiv c_{\vec{R}}^p$, the following conditions must hold:

$$\frac{1}{N}\sum_{\vec{\mathrm{R}}}\sum_{p=1}^{\nu}(\Delta c^{p}_{\vec{\mathrm{R}}})^2=\frac{\bar{c}}{\nu}\left[1-\frac{\bar{c}}{\nu}\right], \tag{25a}$$

$$\sum_{\vec{\kappa}}\sum_{p=1}^{\nu}[\Delta c^{p}(\vec{\kappa})]^2=\frac{\bar{c}}{\nu}\left[1-\frac{\bar{c}}{\nu}\right]. \tag{25b}$$

Equation (25b) means that the random quantities $\Delta c^{p}(\vec{\kappa})$ may take on values only on the surface of the νN-dimensional sphere (the number of allowed $\vec{\kappa}$ points in the Brillouin zone is N) with radius $[(\bar{c}/\nu)(1-\bar{c}/\nu)]^{1/2}$.

However, as was shown in Ref. 10, deviations from the Gaussian behavior for $\vec{\mathrm{u}}_{\vec{\mathrm{R}}}$ are not significant for low concentrations of impurity atoms. Since this is usually the case for interstitial solid solutions, we shall also assume that the distribution of $\vec{\mathrm{u}}_{\vec{\mathrm{R}}}$ is Gaussian.

As soon as this assumption is accepted, the calculation of the averages in Eq. (24) becomes rather simple (see Appendix). Having found the averages we obtain for Eq. (24):

$$\sum_{\vec{\mathrm{q}}'}\sum_{(2)}\left(\alpha^{(2)}_{\vec{\mathrm{q}}'}-e^{-1/2\langle(\vec{\mathrm{q}}'\cdot\Delta\vec{\mathrm{u}}_2)^2\rangle_0}\right)$$

$$\times\langle(\vec{\mathrm{q}}\cdot\Delta\vec{\mathrm{u}}_1)(\vec{\mathrm{q}}'\cdot\Delta\vec{\mathrm{u}}_2)\rangle_0^2=0\,. \tag{24$'$}$$

For the arbitrary function $\Delta\vec{\mathrm{u}}$ the obvious solution is

$$\alpha_{\vec{\mathrm{q}}}(\vec{\mathrm{R}}-\vec{\mathrm{R}}')=e^{-(1/2)\langle[\vec{\mathrm{q}}\cdot(\vec{\mathrm{u}}_{\vec{\mathrm{R}}}-\vec{\mathrm{u}}_{\vec{\mathrm{R}}'})]^2\rangle_0}\,. \tag{26}$$

The result has its counterpart in the self-consistent phonon theory,[4] but now $\vec{\mathrm{u}}_{\vec{\mathrm{R}}}$ are static displacements, not dynamic ones. Note that Eq. (26) was obtained from purely classical considerations for the static system.

The exponential in Eq. (26) may be represented as consisting of two terms:

$$\tfrac{1}{2}\langle[\vec{\mathrm{q}}\cdot(\vec{\mathrm{u}}_{\vec{\mathrm{R}}}-\vec{\mathrm{u}}_{\vec{\mathrm{R}}'})]^2\rangle_0=M_{\vec{\mathrm{q}}}-\Delta M_{\vec{\mathrm{q}}}(\vec{\mathrm{R}}-\vec{\mathrm{R}}')\,,$$

$$M_{\vec{\mathrm{q}}}=\langle(\vec{\mathrm{q}}\cdot\vec{\mathrm{u}}_{\vec{\mathrm{R}}})^2\rangle_0\,,$$

$$\Delta M_{\vec{\mathrm{q}}}(\vec{\mathrm{R}}-\vec{\mathrm{R}}')=\langle(\vec{\mathrm{q}}\cdot\vec{\mathrm{u}}_{\vec{\mathrm{R}}})(\vec{\mathrm{q}}\cdot\vec{\mathrm{u}}_{\vec{\mathrm{R}}'})\rangle_0\,.$$

The first term M_q gives rise to the well-known Debye-Waller factor; the second one, a correlator, decays rather rapidly (though oscillating) with $|\vec{\mathrm{R}}-\vec{\mathrm{R}}'|$. For a disordered solid solution, far from order-disordered transition points, the effect of $\Delta M_{\vec{\mathrm{q}}}(\vec{\mathrm{R}}-\vec{\mathrm{R}}')$ is small compared to that of the Debye-Waller term even for nearest neighbors. With this reservation we shall assume that

$$\alpha_{\vec{\mathrm{q}}}(\vec{\mathrm{R}}-\vec{\mathrm{R}}')\cong\alpha_{\vec{\mathrm{q}}}=\exp[-\langle(\vec{\mathrm{q}}\cdot\vec{\mathrm{u}}_{\vec{\mathrm{R}}})^2\rangle_0]\,. \tag{27}$$

Let us now find the average $\langle(\vec{\mathrm{q}}\cdot\vec{\mathrm{u}}_{\vec{\mathrm{R}}})^2\rangle_0$. From Eqs. (10a) and (10b) we obtain

$$\langle(\vec{\mathrm{q}}\cdot\Delta\vec{\mathrm{u}}_{\vec{\mathrm{R}}})^2\rangle_0=\frac{1}{N}\sum_{\vec{\kappa}}\sum_{p=1}|f_p(\vec{\mathrm{q}},\vec{\kappa})|^2\frac{\bar{c}}{\nu}\left[1-\frac{\bar{c}}{\nu}\right], \tag{28a}$$

where

$$f_p(\vec{\mathrm{q}},\vec{\kappa})=\sum_{\sigma=1}^{3}\frac{[\vec{\mathrm{q}}\cdot\vec{\mathrm{e}}_\sigma(\vec{\kappa})][\vec{\mathrm{e}}_\sigma\cdot\vec{\mathrm{F}}_p(\kappa)]}{m\omega_\sigma^2(\kappa)}\,, \tag{28b}$$

and we made use of the fact that, neglecting the correlations,

$$\langle\Delta c^{p}(\vec{\kappa})\Delta c^{p'}(\vec{\kappa}')\rangle=\frac{\bar{c}}{\nu}\left[1-\frac{\bar{c}}{\nu}\right]\delta_{pp'}\delta_{\vec{\kappa}\vec{\kappa}'}\,. \tag{29}$$

To summarize this section, we have found that the SCHA for static displacements consists in renormalizing the effective interatomic interaction of the "average" host lattice.[11] Namely,

$$\mathscr{U}_{\vec{\mathrm{q}}}\rightarrow e^{-\langle(\vec{\mathrm{q}}\cdot\vec{\mathrm{u}}_{\vec{\mathrm{R}}})^2\rangle_0}\mathscr{U}_{\vec{\mathrm{q}}}\,. \tag{30}$$

This approximation is self-consistent because the phonon spectrum $[\omega_\sigma(\vec{\kappa})]$ of the (average) host lattice that enters $\langle(\vec{\mathrm{q}}\cdot\vec{\mathrm{u}}_{\vec{\mathrm{R}}})^2\rangle_0$ [Eqs. (28a) and (28b)] is itself to be determined via the dynamical matrix $\tilde{\mathscr{A}}^{ij}(\vec{\kappa})$ which, in turn, depends on the Debye-Waller factor,

$$\exp(-M_{\vec{\mathrm{q}}}[\omega])=\exp(-\langle(\vec{\mathrm{q}}\cdot\vec{\mathrm{u}}_{\vec{\mathrm{R}}})^2\rangle_0)\,.$$

For the cubic crystals, Eqs. (28a) and (28b) simplify to

$$\langle(\vec{\mathrm{q}}\cdot\vec{\mathrm{u}}_{\vec{\mathrm{R}}})^2\rangle_0=\frac{\bar{c}}{\nu}\left[1-\frac{\bar{c}}{\nu}\right]q^2$$

$$\times\frac{1}{N}\sum_{\sigma=1}^{3}\sum_{\vec{\kappa}}\sum_{p=1}^{\nu}\left|\frac{[\vec{\mathrm{e}}_\sigma\cdot\vec{\mathrm{F}}_p(\vec{\kappa})]}{m\omega_\sigma^2(\vec{\kappa})}\right|^2. \tag{31}$$

Then the expression for the trace of $\tilde{\mathscr{A}}^{ij}(\vec{\kappa})$ also is easily found:

$$\frac{m}{N}\sum_{\sigma=1}^{3}\sum_{\vec{\kappa}}\omega_\sigma^2(\vec{\kappa})=\frac{\Omega_0}{(2\pi)^3}\int d\vec{\mathrm{q}}\,e^{-q^2\mu[\omega]}q^2\mathscr{U}_{\vec{\mathrm{q}}}$$

$$-\sum_{\vec{\mathrm{g}}}g^2e^{-g^2\mu[\omega]}\mathscr{U}_{\vec{\mathrm{g}}}\,, \tag{32}$$

where $\{\vec{g}\}$ is the set of reciprocal-lattice vectors, and

$$\mu[\omega]=\langle(\vec{u}_{\vec{R}})^2\rangle$$

is the right-hand side of Eq. (31) without the q^2 factor.

IV. LOSS OF STABILITY OF THE INTERSTITIAL SOLID SOLUTION AND LINDEMANN'S CRITERION FOR STATIC DISPLACEMENTS

We are going to show now that the self-consistent equation for the phonon frequencies [either Eq. (32) or Eq. (9) with $\tilde{\mathscr{A}}^{ij}$] contains an instability. For a certain range of parameters involved a real solution for the frequencies does not exist.

In order fo find this range exactly, one must solve Eq. (9) precisely. We shall restrict ourselves to an almost qualitative consideration. Since the results seem to be quite meaningful, we do believe that our consideration is correct, although not being rigorous enough.

Let us introduce the "average" frequency

$$\omega^2=\tfrac{1}{3}\sum_{\sigma=1}^{3}\frac{1}{N}\sum_{\vec{\kappa}}\omega_\sigma^2(\vec{\kappa})\;, \tag{33a}$$

and make use of the so-called Born method,[12] which in our case yields the approximation

$$\frac{1}{\omega^4}=\tfrac{1}{3}\sum_{\sigma=1}^{3}\frac{1}{N}\sum_{\vec{\kappa}}\frac{1}{\omega_\sigma^4(\vec{\kappa})}\;. \tag{33b}$$

Further, since $e_\sigma(\kappa)$ is a unit vector, we set

$$[\vec{e}_\sigma\cdot\vec{F}_p(\vec{\kappa})]=|\vec{F}_p(\vec{\kappa})|\;, \tag{34}$$

and, making use of the theorem of averages, obtain for $\mu[\omega]$ the approximate expression

$$\mu[\omega]=\frac{\bar{c}}{\nu}\left[1-\frac{\bar{c}}{\nu}\right]\frac{f}{m^2\omega^4}\;, \tag{35}$$

where f is a constant.

Equation (32) now reads

$$m\omega^2=\frac{\Omega_0}{(2\pi)^3}\int d\vec{q}\,e^{-\vec{q}^{\,2}\mu[\omega]}q^2\mathscr{U}_{\vec{q}}-\sum_{\vec{g}}e^{-g^2\mu[\omega]}g^2\mathscr{U}_{\vec{g}}\;. \tag{32$'$}$$

Considering $\mu[\omega]$ in Eq. (35) as a variable, Eq. (32′) means

$$\left[\frac{\bar{c}}{\nu}\left[1-\frac{\bar{c}}{\nu}\right]\right]^{1/2}=\phi(\mu)\;, \tag{36a}$$

where

$$\phi(\mu)=\mu^{1/2}f^{1/2}\left[\frac{\Omega_0}{(2\pi)^3}\int d\vec{q}\,e^{-q^2\mu}q^2\mathscr{U}_{\vec{q}}-\sum_{g}e^{-g^2\mu}g^2\mathscr{U}_{\vec{g}}\right]. \tag{36b}$$

Let us consider the behavior of $\phi(\mu)$ at $\mu>0$. $\phi(\mu)$ is obviously a positive quantity [it follows from the definition originating from Eq. (32)]. At $\mu=0$, $\phi(\mu)$ vanishes. At $\mu\to\infty$ the second term of Eq. (36b), the sum over the reciprocal-lattice vectors vanishes when $g^2\mu\gg1$ for all $\vec{g}$. In this range of μ the first term, the integral, may be evaluated using the Laplace method. Since $\mathscr{U}_{\vec{q}}$ is a smooth function, the integral equals

$$\mathscr{U}_{\vec{q}=0}\int d\vec{q}\,q^2e^{-q^2\mu}=\frac{\text{const}}{\mu^{5/2}}$$

and therefore

$$\phi(\mu)\underset{\mu\to\infty}{\longrightarrow}\frac{\text{const}}{\mu^2}\;.$$

At intermediate μ's, $\phi(\mu)$ is obviously undergoing a maximum (or maxima, which is less likely). The shape of $\phi(\mu)$ is shown in Fig. 1.

Let $\mu_{\max}$ correspond to the (strongest) maximum of $\phi(\mu)$. Then Eq. (36) may have a real solution only if

$$\Theta=\left[\frac{\bar{c}}{\nu}\left[1-\frac{\bar{c}}{\nu}\right]\right]^{1/2}\leq\phi(\mu_{\max})\;. \tag{37a}$$

Otherwise only complex μ's may satisfy the equation and that would mean complex frequencies. As one may see from Fig. 1, with the conditions (37a) and (37b) fulfilled, there may be two real solutions for each value of $\bar{c}$. Only the solution $\mu<\mu_{\max}$ has physical meaning.[13] In fact, at $\bar{c}=0$ the static displacements are absent, $\mu=0$, and with increasing $\bar{c}$ the mean-square static displacement μ must increase. The instability arises when

$$\left[\frac{\bar{c}}{\nu}\left[1-\frac{\bar{c}}{\nu}\right]\right]^{1/2}>\phi(\mu_{\max})\;. \tag{37b}$$

The parameter Θ as a function of $\bar{c}/\nu$ has a maximum at $\bar{c}/\nu=\frac{1}{2}$. However, our theory, as was mentioned above, is valid only for low concentrations, definitely for $\bar{c}/\nu<\frac{1}{2}$. Therefore, Θ is the increasing function of $\bar{c}/\nu$, and conditions (37a) and (37b) mean that there exists a limiting concentration of interstitial atoms, above which the sys-

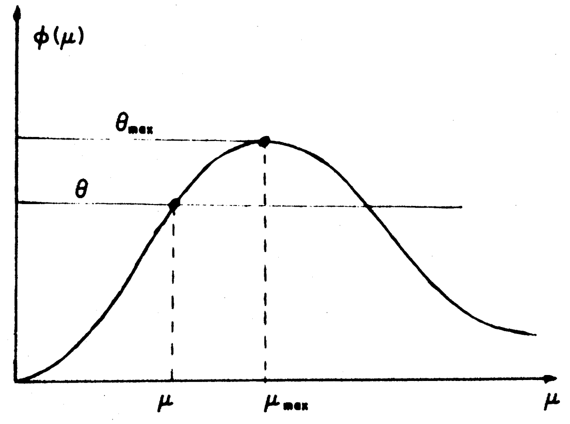

FIG. 1. Possible solutions of Eqs. (36). (Θ_{max},μ_{max}) correspond to the loss of stability point.

tem is dynamically unstable.

The existence of a limiting mean-square static displacement μ_{max} is, in fact, a counterpart of the Lindemann's criterion for melting. In Ref. 7 we pointed out that for substitutional solid solutions the Hume-Rothery rule is also based on the criterion of Lindemann's type.

The general conclusion of our consideration and its graphic interpretation, Fig. 1, obviously do not depend on the approximations [Eqs. (33a), (33b), and (34)] made: The latter only helped in obtaining the result in a simple form. Of course, in order to investigate quantitatively the conditions of the instability and consequently the maximal possible concentration of interstitial atoms, one has to know the value of μ_{max} and the explicit dependence of μ on $\bar{c}$ and other parameters of the system of interest.

According to Lindemann's criteria of melting, $\mu \cong 10^{-2}a^2$ (a is the lattice spacing). In our case μ is probably of the same order of magnitude. As for the explicit expression for μ, we will make use of the one given by Krivoglaz[10,14]:

$$\mu = \langle (u_{\vec{R}})^2 \rangle_0 = \frac{3}{4\pi^2}\frac{\bar{c}}{\nu}\left[1-\frac{\bar{c}}{\nu}\right]a^2\left[\frac{1}{\Omega_0}\frac{\partial\Omega_0}{\partial\bar{c}}\right]^2 A \ . \tag{38}$$

Here A is a factor depending on a combination of elastic moduli but varying only slightly from metal to metal (its typical value is 0.5–1.0; see Table I of Ref. 10).

The relative change of volume,

$$\frac{1}{\Omega_0}\frac{\partial\Omega_0}{\partial\bar{c}} \ ,$$

is the most important parameter in the formula. Its magnitude depends both on the elastic properties of the host lattice and the characteristics of the interstitial atoms. In modern theories of lattice defects this quantity is expressed via the so-called double-force tensor and the Kanzaki model[15]:

$$\frac{1}{\Omega_0}\frac{\partial\Omega_0}{\partial\bar{c}} = \frac{1}{3}\frac{p_{ii}}{\Omega_0 B} \ , \tag{39}$$

where p_{ii} is the trace of the double-force tensor p_{ij}, and B is the bulk modulus of the host lattice.

In the other model, treating an impurity atom as an elastic sphere of radius r_i in the elastic medium, corresponding to a host lattice,[16]

$$\begin{aligned} \frac{1}{\Omega_0}\frac{\partial\Omega_0}{\partial\bar{c}} &= 3\frac{r_i - r_h}{r_i}\chi \ , \\ \chi &= \frac{3(1-\kappa)B_i}{2(1-2\kappa)B + (1+\kappa)B_i} \ , \end{aligned} \tag{40a}$$

where B and B_i are the bulk moduli of the host lattice and the "impurity medium," and κ is the Poisson coefficient. Since for most solids $\kappa = \frac{1}{3}$,

$$\frac{1}{\Omega_0}\frac{\partial\Omega_0}{\partial\bar{c}} = 3\frac{\Delta r_i}{r_i}\frac{3B_i}{B+2B_i} \ . \tag{40b}$$

Here Δr_i is the change of the effective impurity atom radius in the solid solution. We see that Eqs. (40a) and (40b) also have the inverse dependence on the host-lattice bulk modulus B.

Let us return now to the Lindemann's criterion based on Eq. (38):

$$\frac{3}{4\pi}A\frac{\bar{c}}{\nu}\left[1-\frac{\bar{c}}{\nu}\right]\left[\frac{1}{\Omega_0}\frac{\partial\Omega_0}{\partial\bar{c}}\right]^2 = \text{const} \ . \tag{41}$$

The highest possible concentration $\bar{c}$ would correspond to the least value of the volume factor. Considering the transition-metal series corresponding to the fourth and fifth rows of the Periodic Table, one sees that the Wigner-Seitz radius (proportional to any linear dimension of a crystal lattice) undergoes the minima in the centers of the series, while the bulk moduli have maxima in the same points.[17] This is shown in Fig. 2.[18] The average d-electron concentration (DEC) corresponding to these points is DEC=5. As one can see, the Wigner-Seitz radius minima are rather shallow, so that the factor $\Delta r_i/r_i$ changes only slightly, while the bulk moduli maxima are rather sharp. As a result, the least value of the volume factor, Eqs. (33) and (40a), is achieved in the middle of the series for DEC=5. And to the host lattice of such

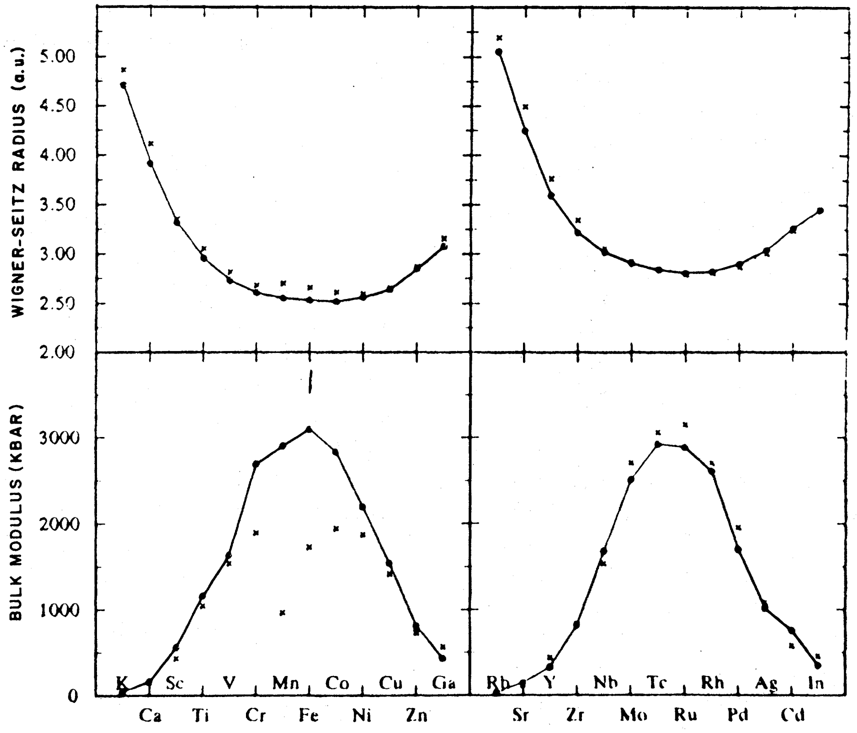

FIG. 2. Wigner-Seitz radius and bulk modulus vs atomic number for 3*d* and 4*d* transition series (Ref. 18). Points and crosses are, respectively, calculated and measured values.

a composition a maximum concentration of interstitial atoms $\bar{c}$ must correspond.

This rule has been recently empirically formulated for metal-hydrogen systems.[19] Examples of such systems are[19,20]

System	DEC
$TiCr_{1.8}H_{3.6}$	5.2
$TiCrMnH_3$	5.0
$Ti_{0.9}Zr_{0.1}CrMnH_3$	5.0
$Ti_{0.8}Zr_{0.2}CrMnH_3$	5.0
$TiFeH_2$	5.0
$TiFe_{0.8}Mn_{0.2}H_2$	4.9

In calculating DEC's for these systems it was assumed that the H atoms contribute their electrons to the *d* bands of the alloys, and the host lattice is the one with the electrons added—which corresponds to our theoretical model, where the host lattice incorporates the effects of the homogeneous distribution of impurity atoms [see Eqs. (4a) and (4b)].

V. CONCLUSION

In this paper we demonstrated that a variational procedure, as applied to either the partition functoin or the Gibbs free energy of the interstitial solid solution with the host atoms displaced from their regular positions, results in an approximation which has typical features of a self-consistent-field theory. The effective potential of the interatomic interaction renormalizes, and as a result, both the atomic static displacements and the phonon frequencies of the "average crystal" have to be found self-consistently.

Of course, the resemblance of the renormalization factor $\alpha_q(R-R')$ with that in the self-consistent phonon theory[4] is due to the Gaussian distribution of displacements. We do believe, however, that the deviation from this distribution making the static displacements different from dynamic ones, does not affect the main feature that the SCHA reveals: an elastic instability of an interstitial solid solution.

The fact that a Lindemann-type criterion must hold for atomic static displacements seems to be quite natural from the physical point of view. As in the case of melting there must be a maximal mean-square static displacement that an alloy can withstand: The crystal as a dynamically stable body collapses if the displacement exceeds a critical value.

The existence of the Lindemann criterion for static displacements might well be postulated (as was the case with the original Lindemann criterion for melting). The DEC rule we explained for metal-hydrogen systems follows directly from this postulate and a realistic model for the displacements—Eq. (41).

As for the proof of the criterion we suggested, it is actually of a semiquantitative character. The approximations involved do not "endanger" the SCHA itself but rather enable us to obtain, in the shortest way, the physically feasible result.

On the other hand, as the calculations have shown,[21] the loss of stability temperature that appears in the self-consistent phonon theory is an order of magnitude higher than the corresponding temperature of melting. The latter is probably due to the fact that the approximation does not allow for uneven anharmonic contributions.[4] This is also the case with the SCHA. We do not know what kind of restrictions are imposed on the static system because of this drawback. A detailed quantitative consideration is necessary in order to learn more about the SCHA. We believe that the SCHA may be useful both for calculations of elastic properties and for an analysis of phase transitions and instabilities due to elastic interaction in solids.

ACKNOWLEDGMENTS

The work was supported by the Ministerium fur Forschung und Technologies and Daimler-Benz AG, Stuttgart, West Germany. I would like to acknowledge the hospitality of the Institute for Theoretical Physics of the University of Tübingen, W. Germany, and fruitful discussions with my colleagues Professor F. A. Wahl, Dr. G. Baumann, and Dr. B. Schapiro. I am also grateful to Dr. O. Bernauer for having drawn my attention to the DEC rule and sending his unpublished paper.

APPENDIX: CALCULATION OF AVERAGES IN THE HARMONIC APPROXIMATION

We need to calculate averages of the following type:

$$A_1 = \langle \Delta u_1^i \Delta u_1^j \Delta u_2^\kappa \Delta u_2^l \rangle_0 ,$$

$$A_2 = \langle \Delta u_1^i \Delta u_1^j \exp[-i(\vec{q}\cdot\Delta\vec{u}_2)] \rangle_0 .$$

A simple method is based on the fact that for Gaussian distribution of displacements,

$$\langle \exp\{i[(\vec{q}_1\cdot\Delta\vec{u}_1)+(\vec{q}_2\cdot\Delta\vec{u}_2)+\cdots+(\vec{q}_n\cdot\Delta\vec{u}_n)]\}\rangle_0 = \exp\{-\tfrac{1}{2}\langle[(\vec{q}_1\cdot\Delta\vec{u}_1)+(\vec{q}_2\cdot\Delta\vec{u}_2)+\cdots+(\vec{q}_n\cdot\Delta\vec{u}_n)]^2\rangle_0\} . \quad \text{(A1)}$$

Then, obviously,

$$\begin{aligned} A_1 &= \frac{\partial^4}{\partial q_1^i \partial q_2^j \partial q_2^\kappa \partial q_2^l} \langle \exp\{-i[(\vec{q}_1\cdot\Delta\vec{u}_1)+(\vec{q}_2\cdot\Delta\vec{u}_2)]\rangle_0\} \Big|_{\vec{q}_1=\vec{q}_2=0} \\ &= \frac{\partial^4}{\partial q_1^i \partial q_1^j \partial q_2^\kappa \partial q_2^l} \exp\{-\tfrac{1}{2}\langle[(\vec{q}_1\cdot\Delta\vec{u}_1)+(\vec{q}_2\cdot\Delta\vec{u}_2)]^2\rangle_0\} \Big|_{\vec{q}_1=\vec{q}_2=0} , \end{aligned} \quad \text{(A2)}$$

$$\begin{aligned} A_2 &= -\frac{\partial^2}{\partial q_1^i \partial q_1^j} \langle \exp\{-i[(\vec{q}_1\cdot\Delta\vec{u}_1)+(\vec{q}_2\cdot\Delta\vec{u}_2)]\}\rangle \Big|_{\vec{q}_1=0} \\ &= -\frac{\partial^2}{\partial q_1^i \partial q_1^j} \exp\{-\tfrac{1}{2}\langle[(\vec{q}_1\cdot\Delta\vec{u}_1)+(\vec{q}_2\cdot\Delta\vec{u}_2)]^2\rangle_0\} \Big|_{\vec{q}_1=0} , \end{aligned} \quad \text{(A3)}$$

and simple algebra gives

$$\langle(\vec{q}\cdot\Delta\vec{u}_1)^2(\vec{q}'\cdot\Delta\vec{u}_2)^2\rangle_0 = 2\langle(\vec{q}\cdot\Delta\vec{u}_1)(\vec{q}'\cdot\Delta\vec{u}_2)\rangle_0^2 + \langle(\vec{q}\cdot\Delta\vec{u}_1)^2\rangle_0\langle(\vec{q}'\cdot\Delta\vec{u}_2)^2\rangle_0 , \quad \text{(A4)}$$

$$\langle(\vec{q}\cdot\Delta\vec{u}_1)^2\exp[i(\vec{q}'\cdot\Delta\vec{u}_2)]\rangle_0 = [\langle(\vec{q}\cdot\Delta\vec{u}_1)^2\rangle_0 - \langle(\vec{q}\cdot\Delta\vec{u}_1)(\vec{q}'\cdot\Delta\vec{u}_2)\rangle_0^2]\exp[-\tfrac{1}{2}\langle(\vec{q}'\cdot\Delta\vec{u}_2)^2\rangle_0] . \quad \text{(A5)}$$

Substituting Eqs. (A4) and (A5) into Eq. (24) one obtains the final result Eq. (24′).

[*] Present address: Institute for Basic Research, 96 Prescott Street, Cambridge, MA 02138.

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[12] See, e.g., Sec. 84 of the paper by G. Leibfried, in *Handbuch der Physik,* edited by S. Flügge (Springer, Berlin, 1955), Vol. VII, Teil 2.

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[16] See J. Friedel, *Dislocations* (Pergamon, New York, 1964), Sec. 3, Chap. 13.

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