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Dynamics of crystals with correlated defect positions

K. H. Weyrich and R. Siems
Theoretische Physik, Universität des Saarlandes, D-6600 Saarbrücken Im Stadtwald,
Federal Republic of Germany

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We present a treatment of crystals containing point defects in which deviations from random defect distributions are taken into account. Known averaging procedures which presuppose randomness of atomic disorder are generalized in order to deal with defect site correlations. The quasicrystalline-approximation-type theory obtained if the pure host crystal is taken as the reference system (which is applicable only to the case of low defect concentrations) is generalized by taking a (random) defect crystal as reference system. This allows a treatment of site-correlation effects also in materials with high defect concentrations. The method is applicable to solid solutions with an arbitrary number of components. For crystals with correlated defect sites, average Green's functions (no atom type specified at any lattice site), and conditionally averaged Green's functions (atom of a specific type—host or defect—at a certain site) are calculated. These two types of Green's functions are then used to determine scattering functions, dispersion curves, and fluctuations at host and defect sites. As a direct application to experiment the method is used to calculate explicitly the change of the polarization of a displacive ferroelectric due to defect site correlations. Realistic correlations are shown to lead to considerable T_c shifts.

I. INTRODUCTION

At present there is a growing interest in systems with atomic disorder, e.g., in crystals whose translational symmetry is disturbed. Important examples of such systems are solids containing point defects. The primary effect of such defects is a change of the normal modes and the eigenvalues of the lattice. While a single defect produces only a localized perturbation of the states (cf., e.g., Refs. 1 and 2) corresponding, e.g., to localized vibrations, a finite concentration influences the global properties of the crystal.[3-8]

The eigenstates of a crystal with many point defects depend on the arrangement of defect positions. Since the latter are not known, since, furthermore, the equations of motion for a special defect arrangement can, in general, not be solved, and since, finally, measurements yield in good approximations quantities averaged over an infinite crystal, one applies averaging procedures like the virtual-crystal-approximation (VCA), the average—T-matrix approximation (ATA), the coherent-potential approximation (CPA), and the quasicrystalline approximation (QCA) (for a review cf. Ref. 9). The basis of these different procedures is the realization that the observed intensive properties of the crystal represent averages, the extensive ones sums over an ensemble of many subscystals into which the original crystal may be divided (the subcrystals being large enough to contain many defects). To calculate these sums and averages the distribution of the defect configurations has to be given. While usually equal probabilities were assumed for all configurations, we shall, in the present paper, consider the influence of deviations from such randomness, i.e., of defect site correlations. We shall assume that the defect distribution is not in thermal equilibrium (i.e., not annealed) with respect to the Hamiltonian employed to describe the lattice dynamics. Rather it is determined "from the outside" by specifying defect site correlations which correspond to additional defect interactions different from those allowed for in the Hamiltonian (quenched nonrandom distribution).[10]

To include these defect site correlations, the established averaging procedures (VCA, ATA, CPA) have to be generalized in such a way as to permit the calculation of the average Green's function for crystals with site-correlated defects. If one starts from the perfect host crystal this procedure leads to a QCA type of equation which is valid only in the limit of small defect concentrations. In the present treatment this restriction is dropped by using a system with a random defect distribution as reference crystal. This leads to a more complicated method for determining the respective Green's functions. From these, quantities like the frequency spectrum may be determined. In addition, conditionally averaged Green's functions are of interest from which, e.g., fluctuations at defect or host positions may be calculated. These are obtained by averaging over those configurations only, in which a certain position is occupied by an atom of a given type. The utilization of these Green's functions is discussed.

In Sec. II the model is presented and the standard averaging methods are discussed. A generalization of the QCA in such a way that the virtual crystal (VC) is used as reference crystal is developed in Sec. III, and conditionally averaged Green's functions are determined in Sec. IV. In Sec. V the general scheme is applied to an anharmonic (ferroelectric) solid solution. The results are discussed in Sec. VI.

II. VCA, ATA, CPA, AND QCA

The Green's function $P_{\vec{m}\,\vec{n},ij}(\omega^2)$ of an ideal, harmonic lattice is defined by

$$\sum_{\vec{n},j}(\phi_{\vec{m}\,\vec{n},ij}-\omega^2 m_i\delta_{\vec{m}\,\vec{n}}\delta_{ij})P_{\vec{n}\,\vec{p},jk}=\delta_{\vec{m}\,\vec{p}}\delta_{ik}\ , \tag{2.1}$$

with force constants $\phi_{\vec{m}\,\vec{n},ij}$ and atomic masses m_i. From now on, scalar lower indices like i which enumerate atomic coordinates within the cells are omitted. The cells are specified by subscripts like $\vec{m}$. For a d-dimensional lattice with s atoms per unit cell, the displacement vector

$$u_{\vec{n}}=(u_{\vec{n},1},\ldots,u_{\vec{n},ds})$$

of the unit cell $\vec{n}$ is thus a vector in a $(d\times s)$-dimensional vector space X_Z. All displacements together form a vector of a vector space $X_R\otimes X_Z$, the dimension of X_R being given by the number N of unit cells.

The influence of defects is described by an additional potential[11] $V_{\vec{m}\,\vec{n}}$. In compact notation the equation of motion for the Green's function of the defect crystal is, then,

$$\sum_{\vec{n}}(\phi_{\vec{m},-\vec{n}}-\omega^2 m\delta_{\vec{m}\,\vec{n}}-V_{\vec{m}\,\vec{n}})G_{\vec{n}\,\vec{p}}=\delta_{\vec{m}\,\vec{p}}\ .$$

$\underline{G}$ and $\underline{P}$ are connected by the Dyson equation

$$\underline{G}=\underline{P}+\underline{PVG}\ . \tag{2.2}$$

For a fixed $\underline{V}$, i.e., for a definite arrangement of defects, $\underline{G}$ could in principle be calculated from Eq. (2.2). For diagonal disorder $\underline{V}$ simplifies to

$$V_{\vec{m}\,\vec{n}}=V_{\vec{m}}\delta_{\vec{m}\,\vec{n}}=V\tau_{\vec{m}}\delta_{\vec{m}\,\vec{n}}\ . \tag{2.3}$$

The defect configuration is specified by the occupation numbers $\tau_{\vec{m}}$ which are 1 if there is a defect at $\vec{m}$ and 0 otherwise. $\langle\underline{G}\rangle$ is obtained from a series expansion of Eq. (2.2) by averaging over all configurations as follows:

$$\langle G_{\vec{m}\,\vec{n}}\rangle=P_{\vec{m}\,\vec{n}}+\sum_{\vec{v}_1}P_{\vec{m}\,\vec{v}_1}\langle V_{\vec{v}_1}\rangle P_{\vec{v}_1\vec{n}}+\sum_{\vec{v}_1,\vec{v}_2}P_{\vec{m}\,\vec{v}_1}\langle V_{\vec{v}_1}P_{\vec{v}_1\vec{v}_2}V_{\vec{v}_2}\rangle P_{\vec{v}_2\vec{n}}+\cdots\ . \tag{2.4}$$

In *VCA* one makes the replacement

$$\langle V_{\vec{v}_1}V_{\vec{v}_2}\cdots V_{\vec{v}_n}\rangle\to\langle V_{\vec{v}_1}\rangle\langle V_{\vec{v}_2}\rangle\cdots\langle V_{\vec{v}_n}\rangle\ . \tag{2.5}$$

For random distributions this is correct up to linear terms in V. In higher-order terms there are deviations: In the quadratic contributions, e.g., the right-hand side of

$$\langle\tau_{\vec{m}}\tau_{\vec{n}}\rangle=c^2-(c^2-c)\delta_{\vec{m}\,\vec{n}}$$

is replaced by c^2, the square of the concentration of defects. Replacing $\underline{P}$ according to Eq. (2.1), making use of the approximation (2.5), and summing the series in Eq. (2.4) one obtains

$$\langle\underline{G}\rangle=[\underline{\phi}-(m\omega^2+\langle V\rangle)\underline{\mathbb{1}}]^{-1}\ , \tag{2.6}$$

with $\langle V_{\vec{v}}\rangle=\langle V\rangle$.

In *ATA*, certain partial sums of Eq. (2.4) are calculated before carrying out the decoupling approximations for the averages. Introducing the one-particle T-matrix

$$t_{\vec{v}_i}=V_{\vec{v}_i}(1-P_{\vec{0}\,\vec{0}}V_{\vec{v}_i})^{-1}$$

(by summing terms with equal subscripts $\vec{v}_i$) and a new Green's function

$$P'_{\vec{m}\,\vec{n}}=P_{\vec{m}\,\vec{n}}-P_{\vec{0}\,\vec{0}}\delta_{\vec{m}\,\vec{n}}$$

(to get rid of a restriction prohibiting successive scattering at the same defect) Eq. (2.4) can be written in powers of $\underline{t}$ as follows:

$$\langle\underline{G}\rangle=\underline{P}+\underline{P}\langle\underline{t}\rangle\underline{P}+\underline{P}\langle\underline{tP't}\rangle\underline{P}\cdots\ . \tag{2.7}$$

A decoupling procedure similar to Eq. (2.5) yields an expression for $\langle\underline{G}\rangle$ which is correct to second order in $\underline{t}$ and at least to the same order in V. Introducing the average T matrix for the interior terms according to

$$\begin{aligned}\langle\underline{t}\rangle+\langle\underline{t}\rangle\underline{P}'\langle\underline{t}\rangle+\cdots&=\langle\underline{t}\rangle(\underline{\mathbb{1}}-\underline{P}'\langle\underline{t}\rangle)^{-1}\\&=\langle\underline{T}\rangle\ ,\end{aligned} \tag{2.8}$$

one obtains (cf. e.g., Ref. 9)

$$\langle \underline{G} \rangle = \{\underline{\phi} - [m\omega^2 + \Sigma(\omega)]\underline{\mathbb{1}}\}^{-1} , \tag{2.9}$$

with

$$\underline{\Sigma} = \langle \underline{T} \rangle (\underline{\mathbb{1}} + \underline{P} \langle \underline{T} \rangle)^{-1} . \tag{2.10}$$

From Eqs. (2.8) and (2.10) one has

$$\Sigma(\omega) = \langle t \rangle (1 + P_{\vec{0}\vec{0}}(\omega) \langle t \rangle)^{-1} . \tag{2.11}$$

With

$$\langle t \rangle = cV(1 - P_{\vec{0}\vec{0}} V)^{-1} \tag{2.12}$$

and Eqs. (2.9) and (2.11), the average Green's function for the defect crystal may be calculated from that of the perfect crystal and the defect potential V. In this approximation the self-energy Σ is a complex number which depends, via $P_{\vec{0}\vec{0}}$, on the frequency. The scattering of phonons at defects is thus taken into account. In contrast to VCA, ATA therefore yields a defect band besides the phonon dispersion of the ideal crystal (if the characteristics of the defects lead to localized vibrations).

The type of ATA discussed above is not symmetric with respect to host and defect atoms and leads to unphysical results for large defect concentrations. This kind of symmetry and an improvement of the approximation is obtained if the virtual crystal is taken as the reference crystal. The original perturbation potential $V_{\vec{m}}$ is replaced by $V_{\vec{m}} - \langle V \rangle$. Thus a host cell is now characterized by a perturbation potential $-\langle V \rangle$ and a defect cell by $V - \langle V \rangle$. In Eq. (2.11) one has to replace $\underline{P}$ by the Green's function $\underline{P}_V$ of the virtual crystal and Eq. (2.12) by

$$\begin{aligned} \langle t \rangle = {} & c(V - \langle V \rangle)[1 - (P_V)_{\vec{0}\vec{0}}(V - \langle V \rangle)]^{-1} \\ & + (1-c)(-\langle V \rangle)[1 + (P_V)_{\vec{0}\vec{0}} \langle V \rangle]^{-1} . \end{aligned} \tag{2.13}$$

This type of ATA yields results which converge for $c \to 0$ and for $c \to 1$ against the exact values. The results of ATA can be improved by replacing, in the expression for the self-energy, the Green's function of the VC self-consistently by the "exact" Green's function (*CPA*).

So far the averages as denoted by angular brackets were always calculated for a distribution with equal probabilities for all configurations. Owing to interactions the defect sites will generally be correlated, however, and these correlations will be different even for crystals of the same composition if their (growth) histories are different—the probability to find a second defect at a specific site in the vicinity of a given defect is thus no longer equal to the average concentration. The deviation from the random distribution is described by a correlation function

$$k^{DD}_{\vec{m}\,\vec{n}} = c^{-2}[\langle \tau_{\vec{m}} \tau_{\vec{n}} \rangle (1 - \delta_{\vec{n}\,\vec{m}}) - \langle \tau_{\vec{m}} \rangle \langle \tau_{\vec{n}} \rangle] . \tag{2.14}$$

$\langle \tau_{\vec{m}} \tau_{\vec{n}} \rangle$ is the probability to find one defect each at $\vec{m}$ and $\vec{n}$. These correlations have to be allowed for when the averages in Eq. (2.7) are calculated. The simple correlation which describes the fact that one lattice site cannot be occupied by two defects was included above (Eq. (2.7) by introducing the Green's function $\underline{P}'$. Correlations with a longer range can be described by a generalization of $\underline{P}'$: Consider one term in Eq. (2.7),

$$\begin{aligned} \langle t_{\vec{m}} P_{\vec{m}\,\vec{n}} t_{\vec{n}} \rangle &= \langle t^2 \tau_{\vec{m}} P_{\vec{m}\,\vec{n}} \tau_{\vec{n}} \rangle \\ &= t^2 \langle \tau_{\vec{m}} \tau_{\vec{n}} \rangle P_{\vec{m}\,\vec{n}} \\ &= \langle \tau \rangle^2 (1 + k^{DD}_{\vec{m}\,\vec{n}}) P_{\vec{m}\,\vec{n}} , \end{aligned} \tag{2.15}$$

with $\langle t \rangle = ct$.

Generalizing the definition of $\underline{P}'$ [cf. the statements above Eq. (2.7)] to

$$P'_{\vec{m}\,\vec{n}} := (1 + k^{DD}_{\vec{m}\,\vec{n}}) P_{\vec{m}\,\vec{n}} , \tag{2.16}$$

the ATA self-energy for correlated defect sites may be written in a form analogous to Eq. (2.11) as follows:

$$\underline{\Sigma} = \langle t \rangle [\underline{\mathbb{1}} + (\underline{P} - \underline{P}') \langle t \rangle]^{-1} . \tag{2.17}$$

The matrix inversion can be performed by means of a Fourier transformation (since $\underline{P}$ and $\underline{P}'$ are invariant with respect to translations in the vector space X_R) and leads to a $\vec{k}$-dependent self-energy as follows:

$$\Sigma(\vec{k}) = \langle t \rangle \{1 + [P(\vec{k}) - P'(\vec{k})] \langle t \rangle\}^{-1} . \tag{2.18}$$

This way of allowing for defect site correlations—the *QCA* (Refs. 12 and 13)—has the advantage of relative simplicity. A severe disadvantage is, however, its asymmetry with respect to the two kinds of atoms. As a consequence it can, similarly as the normal ATA, be applied only in the case of small defect concentrations.

III. GENERALIZATION OF QCA

To obtain a description valid for all concentrations the ATA is carried through with the virtual crystal as host crystal. There are, then, two types of "defects" (1 and 2) with perturbation potentials

$$V^1=V-\langle V\rangle ,$$

and (3.1)

$$V^2=-\langle V\rangle ,$$

two occupation numbers, $\tau^1_{\vec{m}}$ and $\tau^2_{\vec{m}}$, and four correlation functions,

$$k^{\mu\nu}_{\vec{m}\,\vec{n}}=\frac{1}{c^\mu c^\nu}[\langle\tau^\mu_{\vec{m}}\tau^\nu_{\vec{n}}\rangle(1-\delta_{\vec{m}\,\vec{n}})-\langle\tau^\mu_{\vec{m}}\rangle\langle\tau^\nu_{\vec{n}}\rangle] , \tag{3.2}$$

with $\mu,\nu=1,2$ and

$$\tau^2_{\vec{m}}=1-\tau^1_{\vec{m}} . \tag{3.3}$$

Assuming inversion symmetry, one has

$$k^{21}_{\vec{m}\,\vec{n}}=k^{12}_{\vec{m}\,\vec{n}} .$$

Owing to Eq. (3.3) the correlation functions $k_{\vec{m}\,\vec{n}}$ are interdependent:

$$(c^1)^2k^{11}_{\vec{m}\,\vec{n}}=(c^2)^2k^{22}_{\vec{m}\,\vec{n}}$$

and

$$c^2k^{12}_{\vec{m}\,\vec{n}}=-c^1k^{11}_{\vec{m}\,\vec{n}} . \tag{3.4}$$

In Eq. (2.7) $\underline{P}$ is now the Green's function of the virtual crystal. The equations $t_{\vec{m}}=t\tau_{\vec{m}}$ for the one-particle T matrices have to be replaced by

$$t_{\vec{m}}=\sum_{\nu=1}^{2}t^\nu\tau^\nu_{\vec{m}} , \tag{3.5}$$

with $t^\nu=V^\nu(1-P_{\vec{0}\,\vec{0}}V^\nu)^{-1}$.

A decoupling procedure analogous to Eq. (2.15) leads to a generalized $\underline{P}'$: From

$$\langle t_{\vec{m}}P_{\vec{m}\,\vec{n}}t_{\vec{n}}\rangle=\sum_{\mu,\nu=1}^{2}t^\nu t^\mu P_{\vec{m}\,\vec{n}}\langle\tau^\mu_{\vec{m}}\tau^\nu_{\vec{n}}\rangle ,$$

one obtains, with $\langle t^\nu\rangle=t^\nu c^\nu$,

$$\langle t_{\vec{m}}P_{\vec{m}\,\vec{n}}t_{\vec{n}}\rangle=\sum_{\mu,\nu=1}^{2}\langle t^\mu\rangle\langle t^\nu\rangle P_{\vec{m}\,\vec{n}}(k^{\mu\nu}_{\vec{m}\,\vec{n}}+1) . \tag{3.6}$$

The two kinds of defects define a two-dimensional vector space X_S. Characterizing matrices in X_S by a bar [e.g., $(k^{\mu\nu})=\bar{k}$] and defining

$$\begin{aligned}S(\bar{A})&:=\sum_{\mu,\nu=1}^{2}A^{\nu\mu} ,\\ \langle\bar{t}\rangle&:=\begin{bmatrix}\langle t^1\rangle & 0\\ 0 & \langle t^2\rangle\end{bmatrix} ,\\ \bar{P}_{\vec{m}\,\vec{n}}&:=[P^{\mu\nu}_{\vec{m}\,\vec{n}}]=[P_{\vec{m}\,\vec{n}}(k^{\mu\nu}_{\vec{m}\,\vec{n}}+1)] ,\end{aligned} \tag{3.7}$$

one obtains from Eq. (3.6),

$$\langle t_{\vec{m}}P_{\vec{m}\,\vec{n}}t_{\vec{n}}\rangle=S(\langle\bar{t}\rangle\bar{P}\langle\bar{t}\rangle) ,$$

and from Eq. (2.7),

$$\langle\underline{G}\rangle=\underline{P}+\underline{P}S(\langle\bar{t}\rangle+\langle\bar{t}\rangle\underline{\bar{P}}\langle\bar{t}\rangle+\cdots)\underline{P} . \tag{3.8}$$

The average T matrix for the whole crystal is thus

$$\begin{aligned}\langle\underline{T}\rangle&=S\left[\langle\bar{t}\rangle\sum_{n=0}^{\infty}(\underline{\bar{P}}\langle\bar{t}\rangle)^n\right]\\ &=S(\langle\bar{t}\rangle(\underline{\mathbb{1}}-\underline{\bar{P}}\langle\bar{t}\rangle)^{-1}) .\end{aligned}$$

Since the elements of the 2×2 matrix

$$\underline{\mathbb{1}}-\underline{\bar{P}}\langle\bar{t}\rangle=\begin{Bmatrix}\underline{\mathbb{1}}-\underline{P}^{11}\langle t^1\rangle & -\underline{P}^{12}\langle t^2\rangle\\ -\underline{P}^{21}\langle t^1\rangle & \underline{\mathbb{1}}-\underline{P}^{22}\langle t^2\rangle\end{Bmatrix} \tag{3.9}$$

are themselves matrices one has to retain the sequence of multiplications upon forming the inverse. Confining ourselves from now on to cases where commutivity is guaranteed[14] (e.g., Bravais lattices with cubic perturbations, crystals with one coordinate per unit cell) we obtain

$$\begin{aligned}\langle\underline{T}\rangle=\underline{D}^{-1}[&\langle t^1\rangle\underline{\mathbb{1}}+\langle t^2\rangle\underline{\mathbb{1}}\\ &-\langle t^1\rangle\langle t^2\rangle(\underline{P}^{11}+\underline{P}^{22}-2\underline{P}^{12})] ,\end{aligned} \tag{3.10}$$

with

$$\begin{aligned}\underline{D}=(&\underline{\mathbb{1}}-\underline{P}^{11}\langle t^1\rangle)(\underline{\mathbb{1}}-\underline{P}^{22}\langle t^2\rangle)\\ &-\underline{P}^{12}\langle t^1\rangle\underline{P}^{12}\langle t^2\rangle .\end{aligned}$$

$\underline{\Sigma}$ can be calculated from Eqs. (2.10) and (3.10).

Since this involves the inversion of translation-invariant matrices the explicit result is derived in $\vec{k}$ representation:

$$\Sigma(\vec{k})=N^{-1}(\vec{k})\{\langle t^1\rangle+\langle t^2\rangle-\langle t^1\rangle\langle t^2\rangle[P^{11}(k)+P^{22}(k)-2P^{12}(k)]\} , \tag{3.11}$$

with

$$\begin{aligned}N(\vec{k})=\;&1-P^{11}\langle t^1\rangle-P^{22}\langle t^2\rangle+\langle t^1\rangle\langle t^2\rangle(P^{11}P^{22}-P^{12}P^{12})\\ &+(\langle t^1\rangle+\langle t^2\rangle)P-\langle t^1\rangle\langle t^2\rangle(P^{11}-2P^{12}+P^{22})P .\end{aligned}$$

There are two special cases for which Eq. (3.11) is reduced to previous results:

(1) The reference crystal is, as before, the pure host crystal with the Green's function $\underline{P}$. Then one has $\langle t^2 \rangle = 0$, $\langle t^1 \rangle = \langle t \rangle$, and $\underline{P}^{11} = \underline{P}'$. The self-energy expression (3.11) is then reduced to Eq. (2.18).

(2) The correlations vanish for $\vec{\mathrm{m}} \neq \vec{\mathrm{n}}$. Then $P^{\mu\nu} = P'$ for all μ,ν and one obtains from Eq. (3.11) the expression of Eq. (2.11) with the one-particle T matrix of Eq. (2.13):

$$\Sigma(k) = \frac{\langle t^1 \rangle + \langle t^2 \rangle}{1 + (\langle t^1 \rangle + \langle t^2 \rangle)[P(\vec{\mathrm{k}}) - P'(\vec{\mathrm{k}})]} \;.$$

The self-energy in Eq. (3.11) is symmetric in both types of atoms and yields the former result for small concentrations. Another advantage of the method just described is that it can directly be extended to solid solutions with more than two components.

Incidentally, quite a different possibility to allow for defect site correlations is to start from the generalization of the CPA introduced in Refs. 15 and 16 to handle defect clusters, and then to establish specific pair correlations by giving appropriate weights to the different cluster configurations.

IV. INCLUSION OF DEFECT SITE CORRELATIONS: CONDITIONALLY AVERAGED GREEN'S FUNCTIONS

The Green's functions obtained so far were calculated by averaging—with different weights—over all cell configurations; no lattice site was distinguished from the others. However, for some purposes (e.g., for the calculation of the fluctuation at a defect site) conditionally averaged Green's functions $\langle \Gamma^{\vec{\mathrm{i}},\nu}_{\vec{\mathrm{m}}\,\vec{\mathrm{n}}} \rangle$ are needed which are formed by averaging over those configurations only, in which a given site $\vec{\mathrm{i}}$ is occupied by an atom of type ν.

For random distribution of defects, $\langle \Gamma^{\vec{\mathrm{i}},\nu}_{\vec{\mathrm{m}}\,\vec{\mathrm{n}}} \rangle$ can easily be determined from $\langle G_{\vec{\mathrm{n}}\,\vec{\mathrm{m}}} \rangle$ by introducing, at position $\vec{\mathrm{i}}$, a defect of strength $V = V^\nu - \Sigma$ into a system described by $\langle G_{\vec{\mathrm{m}}\,\vec{\mathrm{n}}} \rangle$. This corresponds to a single defect in a translationally invariant lattice. One obtains

$$\langle \Gamma^{\vec{\mathrm{i}},\nu}_{\vec{\mathrm{m}}\,\vec{\mathrm{n}}} \rangle = \langle G_{\vec{\mathrm{m}}\,\vec{\mathrm{n}}} \rangle + \langle G_{\vec{\mathrm{m}}\,\vec{\mathrm{i}}} \rangle \times \frac{V^\nu - \Sigma}{1 - (V^\nu - \Sigma)\langle G_{\vec{\mathrm{i}}\,\vec{\mathrm{i}}} \rangle} \langle G_{\vec{\mathrm{i}}\,\vec{\mathrm{n}}} \rangle \;. \tag{4.1}$$

This is no longer true if the defect sites are correlated, since then the distribution in the vicinity of $\vec{\mathrm{i}}$ is altered.

A different way of calculating $\langle \Gamma^{\vec{\mathrm{i}},\nu}_{\vec{\mathrm{m}}\,\vec{\mathrm{n}}} \rangle$ is to admit explicitly only those configurations in the averaging process in Eq. (2.7) in which position $\vec{\mathrm{i}}$ is occupied by a ν-type atom. Such averages will be indicated by superscripts ν, $\vec{\mathrm{i}}$ on the angular brackets. To begin with, the principle of the subsequent calculation will again be explained for that method in which a crystal consisting of one type of atoms only (e.g., type 2) is taken as the reference crystal. One has thus to determine

$$\begin{aligned}\langle \Gamma^{1,\vec{\mathrm{i}}} \rangle &= \langle G \rangle^{1,\vec{\mathrm{i}}} \\ &= \underline{P} + \underline{P}\langle \underline{t} \rangle^{1,\vec{\mathrm{i}}}\underline{P} \\ &\quad + \underline{P}\langle \underline{t}\underline{P}'\underline{t} \rangle^{1,\vec{\mathrm{i}}}\underline{P} + \cdots \;.\end{aligned} \tag{4.2}$$

Defining a new T matrix,

$$\underline{\tilde{t}} := \underline{t} - \underline{\Theta}^i, \quad \text{with } t_{\vec{\mathrm{m}}\,\vec{\mathrm{n}}} := t_{\vec{\mathrm{m}}}\,\delta_{\vec{\mathrm{m}}\,\vec{\mathrm{n}}} \;,$$

and (4.3)

$$\begin{aligned}\Theta^{\vec{\mathrm{i}}}_{\vec{\mathrm{m}}\,\vec{\mathrm{n}}} &= (t_{\vec{\mathrm{i}}} - \langle t \rangle)\delta_{\vec{\mathrm{m}}\,\vec{\mathrm{i}}}\,\delta_{\vec{\mathrm{m}}\,\vec{\mathrm{n}}} \\ &\quad + \langle t \rangle k^{DD}_{\vec{\mathrm{n}}\,\vec{\mathrm{i}}}(1 - \delta_{\vec{\mathrm{n}}\,\vec{\mathrm{i}}})\delta_{\vec{\mathrm{m}}\,\vec{\mathrm{n}}} \;,\end{aligned}$$

i.e., $\langle \underline{\tilde{t}} \rangle^{1,\vec{\mathrm{i}}} = \langle \underline{t} \rangle$, one obtains by introducing $\underline{t}$ from Eq. (4.3) into Eq. (4.2)

$$\begin{aligned}\langle \underline{\Gamma}^{1,\vec{\mathrm{i}}} \rangle &= \underline{P} + \underline{P}\langle \underline{t} \rangle \underline{P} + \underline{P}\Theta^{\vec{\mathrm{i}}}\underline{P} + \underline{P}\langle \underline{t} \rangle \underline{P}'\langle \underline{t} \rangle \underline{P} + \underline{P}\underline{\Theta}^{\vec{\mathrm{i}}}\underline{P}'\langle \underline{t} \rangle \underline{P} \\ &\quad + \underline{P}\langle \underline{t} \rangle \underline{P}'\underline{\Theta}^{\vec{\mathrm{i}}}\underline{P} + \underline{P}\langle \underline{t} \rangle \underline{P}'\langle \underline{t} \rangle \underline{P}'\langle \underline{t} \rangle \underline{P} + \cdots \;,\end{aligned} \tag{4.4}$$

where use has been made of Eqs. (2.15) and (2.16). Observing that the sum of all terms containing no factor $\Theta^{\vec{\mathrm{i}}}$ is $\langle G \rangle$ and introducing

$$\sum_{l=0}^{\infty} (\langle t \rangle \underline{P}')^l := \underline{R}, \quad \text{and} \quad \sum_{l=0}^{\infty} (\underline{P}'\langle t \rangle)^l := \underline{L} \;,$$

one has

$$\begin{aligned}\langle \underline{\Gamma}^{1,\vec{i}}\rangle &= \langle \underline{G}\rangle + \underline{PR}\underline{\Theta}^{\vec{i}}(\underline{\mathbb{1}} + \underline{P}'\underline{\Theta}^{\vec{i}} + \underline{P}'\langle t\rangle \underline{P}'\underline{\Theta}^{\vec{i}} + \underline{P}'\underline{\Theta}^{\vec{i}}\underline{P}'\underline{\Theta}^{\vec{i}})\underline{LP} \\ &= \langle \underline{G}\rangle + \underline{PR}\underline{\Theta}^{\vec{i}}(\underline{\mathbb{1}} + \underline{P}'\underline{R}\underline{\Theta}^{\vec{i}} + \underline{P}'\underline{R}\underline{\Theta}^{\vec{i}}\underline{P}'\underline{R}\underline{\Theta}^{\vec{i}} + \cdots)\underline{LP}\ . \end{aligned} \tag{4.5}$$

Summing the different geometric series, one obtains

$$\langle \underline{\Gamma}^{1,\vec{i}}\rangle = \langle \underline{G}\rangle + \underline{PR}\underline{\Theta}^{\vec{i}}(\underline{1} - \underline{P}'\underline{R}\underline{\Theta}^{\vec{i}})^{-1}\underline{LP}\ , \tag{4.6}$$

with

$$\underline{R} = (\underline{1} - \langle t\rangle \underline{P}')^{-1},\ \ \underline{L} = (1 - \underline{P}'\langle t\rangle)^{-1}\ . \tag{4.7}$$

The relevant part $\underline{U}$ of the inverse of the expression in parentheses in Eq. (4.6) is

$$\underline{U}^{\vec{i}} = \begin{bmatrix} 0 & & 0 \\ & \underline{\mathbb{1}}\,|\,X_K & \\ 0 & & 0 \end{bmatrix} + \begin{bmatrix} 0 & & 0 \\ & \underline{P}'\underline{R}\underline{\Theta}^{\vec{i}}\,|\,X_K & \\ 0 & & 0 \end{bmatrix} + \cdots = \begin{bmatrix} 0 & & 0 \\ & (\underline{\mathbb{1}}\,|\,X_K - \underline{P}'\underline{R}\underline{\Theta}^{\vec{i}}\,|\,X_K)^{-1} & \\ 0 & & 0 \end{bmatrix}\ , \tag{4.8}$$

where $\underline{M}\,|\,X_K$ means the reduction of matrix $\underline{M}$ to that subspace X_K of X_R for which there are nonzero diagonal elements of $\underline{\Theta}^{\vec{i}}$. Thus one finally has

$$\langle \underline{\Gamma}^{\nu,\vec{i}}\rangle = \langle \underline{G}\rangle + \underline{PR}\underline{\Theta}^{\vec{i}}\underline{U}^{\vec{i}}\underline{LP}\ , \tag{4.9}$$

with $\underline{R}$, $\underline{L}$, and $\underline{U}^{\vec{i}}$ given by Eqs. (4.7) and (4.8). In the Appendix it is shown that for uncorrelated defects Eq. (4.9) reduces, as it should, to Eq. (4.1) which was obtained above in a different way.

If the virtual crystal is taken as the reference crystal the conditionally averaged Green's functions are derived in a similar way. In analogy to Eq. (4.3) we define

$${}^{\nu}\bar{\underline{\Theta}}^{\vec{i}} = {}^{\nu}\underline{\Theta}^{1,\vec{i}} \otimes \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} + {}^{\nu}\underline{\Theta}^{2,\vec{i}} \otimes \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix}\ , \tag{4.10}$$

with

$${}^{\nu}\Theta^{\mu,\vec{i}}_{\vec{n}\,\vec{m}} = [(t^{\mu}\delta_{\mu\nu} - \langle t^{\mu}\rangle)\delta_{\vec{n}\,\vec{i}} + \langle t^{\mu}\rangle k^{\mu\nu}_{\vec{n}\,\vec{i}}(1 - \delta_{\vec{n}\,\vec{i}})]\delta_{\vec{n}\,\vec{m}}\ .$$

The result corresponding to Eq. (4.9) is obtained by modifying the derivation of the latter correspondingly and by replacing $\langle t\rangle$, $\underline{R}$, $\underline{L}$, $\underline{P}'$, and $\underline{\Theta}^{\vec{i}}$ by $\langle \bar{t}\rangle$, $\bar{\underline{R}} = (1 - \langle \bar{t}\rangle \bar{\underline{P}})^{-1}$, $\bar{\underline{L}} = (1 - \bar{\underline{P}}\langle \bar{t}\rangle)^{-1}$, $\bar{\underline{P}}$, and ${}^{\nu}\bar{\underline{\Theta}}^{\vec{i}}$, respectively,

$$\langle \underline{\Gamma}^{\nu,\vec{i}}\rangle = \langle \underline{G}\rangle + \underline{PS}(\bar{\underline{R}}\,{}^{\nu}\bar{\underline{\Theta}}^{\vec{i}}\,{}^{\nu}\bar{\underline{U}}^{\vec{i}}\,\bar{\underline{L}})\underline{P}\ , \tag{4.11}$$

with

$${}^{\nu}\bar{\underline{U}}^{\vec{i}} = \begin{bmatrix} 0 & & 0 \\ & (\underline{\mathbb{1}}\,|\,X_K \otimes X_S - \bar{\underline{P}}\bar{\underline{R}}\,{}^{\nu}\bar{\underline{\Theta}}^{\vec{i}}\,|\,X_K \otimes X_S)^{-1} & \\ 0 & & 0 \end{bmatrix}\ .$$

S is defined below Eq. (3.6).

We shall now explicitly perform the matrix inversion, confining ourselves, however, to cases in which the matrices $\langle t\rangle$ and $\underline{P}$ commute in X_Z. (The calculation can also be carried through if this is not the case, but it is then rather long-winded.) One obtains

$$\bar{\underline{R}} = \underline{D}_R^{-1}\begin{bmatrix} \underline{1} - \langle t^2\rangle \underline{P}^{22} & \langle t^1\rangle \underline{P}^{12} \\ \langle t^2\rangle \underline{P}^{12} & \underline{1} - \langle t^1\rangle \underline{P}^{11} \end{bmatrix}\ , \tag{4.12}$$

with

$$\underline{D}_R = (1 - \langle t^1\rangle \underline{P}^{11})(\underline{1} - \langle t^2\rangle \underline{P}^{22}) - \langle t^1\rangle \langle t^2\rangle \underline{P}^{12}\underline{P}^{12}\ .$$

$\underline{D}_R$ can be diagonalized in $\vec{k}$ space since it is invariant with respect to lattice translations. The matrix elements of $\underline{R}^{\nu\mu}$ are expressed as Fourier integrals over the Brillouin zone (BZ) of the lattice as follows:

$$R^{11}_{\vec{\mathrm{m}}\,\vec{\mathrm{n}}}=\frac{V_Z}{(2\pi)^d}\int_{\mathrm{BZ}} d\vec{\mathrm{k}}[1-\langle t^2\rangle P^{22}(\vec{\mathrm{k}})]e^{i\vec{\mathrm{k}}\cdot(\vec{\mathrm{m}}-\vec{\mathrm{n}})a}/N(\vec{\mathrm{k}})\ , \tag{4.13}$$

with

$$N(k)=[1-\langle t^1\rangle P^{11}(k)][1-\langle t^2\rangle P^{22}(k)]-\langle t^1\rangle\langle t^2\rangle P^{12}(k)P^{12}(k)\ .$$

V_Z is the volume of the unit cell and a the lattice constant. The other $\underline{R}^{\nu\mu}$ are obtained in an analogous way. One further has

$$\underline{L}^{\nu\mu}=\underline{R}^{\mu\nu}\ . \tag{4.14}$$

The matrix product $\overline{\underline{PR}}=\overline{\underline{A}}$ occuring in Eq. (4.11) is derived similarly:

$$A^{21}_{\vec{\mathrm{m}}\,\vec{\mathrm{n}}}=A^{12}_{\vec{\mathrm{m}}\,\vec{\mathrm{n}}}=\frac{V_Z}{(2\pi)^d}\int_{\mathrm{BZ}} d\vec{\mathrm{k}}\,P^{12}e^{i\vec{\mathrm{k}}\cdot(\vec{\mathrm{m}}-\vec{\mathrm{n}})a}/N(\vec{\mathrm{k}})\ , \tag{4.15}$$

$$A^{11}_{\vec{\mathrm{m}}\,\vec{\mathrm{n}}}=\frac{V_Z}{(2\pi)^d}\int_{\mathrm{BZ}} d\vec{\mathrm{k}}[(1-\langle t^2\rangle P^{22})P^{11}+\langle t^2\rangle(P^{12})^2]e^{i\vec{\mathrm{k}}\cdot(\vec{\mathrm{m}}-\vec{\mathrm{n}})a}/N(\vec{\mathrm{k}})\ . \tag{4.16}$$

A^{22} is obtained by interchanging 1 and 2.

Making use of Eq. (4.14) and of the definition

$$\overline{{}^{\nu}\underline{g}}:={}^{\nu}\overline{\underline{\Theta}}^{\vec{\mathrm{i}}}\,|_{X_S\otimes X_K}\,{}^{\nu}\overline{\underline{U}}^{\vec{\mathrm{i}}}\ ,$$

Eq. (4.11) may be written in the compact form

$$\langle\Gamma^{\vec{\mathrm{i}},\nu}\rangle=\langle G\rangle+\underline{P}\sum_{\mu,\rho,\kappa,\sigma=1}^{2}\underline{R}^{\mu\rho}\,{}^{\nu}\underline{g}^{\rho\kappa}\,\underline{R}^{\sigma\kappa}\underline{P}\ . \tag{4.17}$$

This is an expression for the conditionally averaged Green's function which takes defect site correlations into account and which can be used for concentrations in the whole range from 0 to 1. For a given situation the integrals (4.13), (4.15), and (4.16) and the inverse of the matrix $(\mathbb{1}-\overline{\underline{A}}\,{}^{\nu}\overline{\underline{\Theta}}^{\vec{\mathrm{i}}})\,|_{X_S\otimes X_K}$ have to be determined (numerically, if necessary). The dimension of the latter is $h=2(Z+1)$ where Z is the number of lattice sites connected by nonzero correlations with the lattice site $\vec{\mathrm{i}}$. With the help of Eqs. (3.11) and (4.17) the CPA crystal for randomly distributed defects may be used, instead of the virtual crystal, as reference crystal.

V. APPLICATION TO FERROELECTRIC CRYSTALS WITH SITE-CORRELATED DEFECTS

In this section the results of the previous sections are used to calculate the influence of the defect site statistics on the macroscopically measurable polarization curve of displacive ferroelectrics and on dispersion curves. The calculations will be performed by making use of the conditionally averaged Green's functions determined in Sec. IV. The system is described by the Hamiltonian

$$H=\sum_{\vec{\mathrm{n}}}\frac{p^2_{\vec{\mathrm{n}}}}{2m(1+\epsilon\tau^1_{\vec{\mathrm{n}}})}+\tfrac{1}{2}(A+\Delta A\tau^1_{\vec{\mathrm{n}}})x^2_{\vec{\mathrm{n}}}+\tfrac{1}{4}(B+\Delta B\tau^1_{\vec{\mathrm{n}}})x^4_{\vec{\mathrm{n}}}+\tfrac{1}{2}\sum_{\vec{\mathrm{n}},\vec{\mathrm{m}}}W_{\vec{\mathrm{n}}\,\vec{\mathrm{m}}}x_{\vec{\mathrm{n}}}x_{\vec{\mathrm{m}}}\ , \tag{5.1}$$

where $\vec{\mathrm{x}}_{\vec{\mathrm{n}}}$ $(p_{\vec{\mathrm{n}}})$ is the local normal coordinate (momentum) connected with the soft mode. The harmonic interaction $W_{\vec{\mathrm{n}}\,\vec{\mathrm{m}}}$ has long- and short-range contributions.

By means of the self-consistent phonon approximation (SCPA) the problem is reduced to the solution of a system of equations for the average displacements $\langle x_{\vec{\mathrm{n}}}\rangle$ and the harmonic fluctuations $\langle u^2_{\vec{\mathrm{n}}}\rangle$ about them. The range of validity of SCPA has been discussed by several authors[17–19]: For a system described by the Hamiltonian (5.1) the actual phase transition is continuous. While for a short-range interaction SCPA leads to a first-order transition, it yields for systems containing also a long-range interaction regions in the potential parameter space with second-order transitions (II) as well as regions with first-order transitions (I). A numerical comparison, for a system without defects,[17] shows that in the region II there is a good quantitative agreement between SCPA and molecular dynamics (MD) results. MD calculations[18] demonstrate that even for values of the potential parameters well within region I there are only small deviations between MD and SCPA results (except, of course, in direct vicinity of the transition). In

Fig. 1, for example, polarization curves obtained by SCPA are compared with results of MD calculations. Similar results were obtained for systems with pure short-range interaction.[19] In Ref. 19 the temperature range is determined for which SCPA yields reliable results.

The autocorrelation function is connected with the Green's function by

$$\langle u_{\vec{n}}^2 \rangle = k_B T \,\mathrm{Re} G_{\vec{n}\vec{n}}(\omega^2=0) \,. \tag{5.2}$$

$G_{\vec{n}\vec{m}}$ is the Green's function corresponding to an effective harmonic Hamiltonian with the potential constants

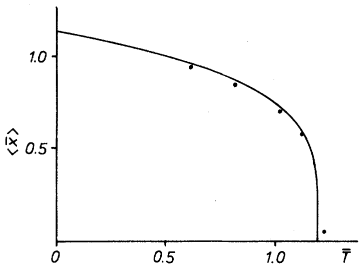

FIG. 1. Polarization of a one-dimensional crystal without defects vs temperature. The curve represents the SCPA result, the dots were calculated with MD. The SCPA curve varies discontinuously near T_c. The parameters are defined in Fig. 2 and have the values $\bar{A}=2.14$, $\bar{\Lambda}=8$.

$$\Phi_{\vec{n}\vec{m}} = \delta_{\vec{n}\vec{m}} [A + \Delta A \tau_{\vec{n}}^1 + 3(B + \Delta B \tau_{\vec{n}}^1)(\langle x_{\vec{n}} \rangle^2 + \langle u_{\vec{n}}^2 \rangle)] + W_{\vec{n}\vec{m}} \,. \tag{5.3}$$

The system of equations is completed by the relations

$$[A + \Delta A \tau_{\vec{n}}^1 + 3(B + \Delta B \tau_{\vec{n}}^1)\langle u_{\vec{n}}^2 \rangle]\langle x_{\vec{n}} \rangle + (B + \Delta B \tau_{\vec{n}}^1)\langle x_{\vec{n}} \rangle^3 + \sum_{\vec{m}} W_{\vec{n}\vec{m}} \langle x_{\vec{m}} \rangle = 0 \,, \tag{5.4}$$

connecting the average displacements with the fluctuations.

These equations, which describe the ferroelectric crystal for a fixed configuration of defect positions, are averaged in a way similar to that introduced in Ref. 6 over all such configurations. Now, however, defect site correlations are taken into account. The averaged fluctuations at defect and host positions are obtained from the conditionally averaged Green's function given in Eq. (4.17):

$$\langle\langle (u^\nu)^2 \rangle\rangle = k_B T \,\mathrm{Re} \langle \Gamma_{0\,0}^{\vec{0},\nu} \rangle \quad \text{for } \nu = 1,2 \,, \tag{5.5}$$

where the double angular brackets imply an averaging, over all defect configurations, of thermal averages. The mean fluctuations $\langle\langle (u^\nu)^2 \rangle\rangle$ at host and defect positions are connected with the mean displacements $\langle\langle x^\nu \rangle\rangle$ at host and defect positions by the averaged form of Eq. (5.4):

$$\sum_{\vec{m}} W_{\vec{0}\vec{m}} (w_{\vec{0}\vec{m}}^{\nu 1} \langle\langle x^1 \rangle\rangle + w_{\vec{0}\vec{m}}^{\nu 2} \langle\langle x^2 \rangle\rangle) + [A + \Delta A \delta_{1\nu} + 3(B + \Delta B \delta_{1\nu}) \langle\langle (u^\nu)^2 \rangle\rangle] \langle\langle x^\nu \rangle\rangle$$
$$+ (B + \Delta B \delta_{1\nu}) \langle\langle x^\nu \rangle\rangle^3 = 0, \quad \text{for } \nu = 1 \text{ and } 2 \,. \tag{5.6}$$

Here $w_{\vec{n}\vec{m}}^{\nu\mu} = c^\mu (k_{\vec{n}\vec{m}}^{\nu\mu} + 1)$ is the conditional probability to find a μ-type atom at position $\vec{m}$ if a ν-type atom is at $\vec{n}$.

In the calculation of $\langle \Gamma_{0\,0}^{\vec{0},\nu} \rangle$ it is assumed that also the indirect change of the potential by the defects via the fluctuations and mean displacements is local:

$$\Phi_{\vec{n}\vec{m}} = \delta_{\vec{n}\vec{m}} (A + \Delta A \tau_{\vec{n}}^1 + 3(B + \Delta B \tau_{\vec{n}}^1) \{ [\langle\langle x^1 \rangle\rangle^2 + \langle\langle (u^1)^2 \rangle\rangle] \tau_{\vec{n}}^1 + [\langle\langle x^2 \rangle\rangle^2 + \langle\langle (u^2)^2 \rangle\rangle] \tau_{\vec{n}}^2 \}) + W_{\vec{n}\vec{m}} \,. \tag{5.7}$$

With the help of Eq. (5.5)–(5.7) we are in a position to calculate the polarization of a ferroelectric solid solution with site correlation. For explicit calculations the interaction $W_{\vec{n}\vec{m}}$ is split into a nearest-neighbor (NN) part J with cubic symmetry and a long-range part $\lambda f(\vec{n}-\vec{m})$. The latter is expanded in a Fourier series and only the $\vec{k}=\vec{0}$ term $\Lambda = \lambda \hat{f}(\vec{k}=\vec{0})$ is considered. The system of equations (5.5) and (5.6), with the potential (5.7), is solved numerically (by Newton iteration) for several temperatures.

In Fig. 2 the polarization of a three-dimensional crystal containing 10% defects is shown for different NN correlations $K = 3(c_1)^2 k_{0\,\vec{n}}^{11}$ (with cubic symmetry). We obtain a marked increase of the polarization and of the critical temperature with in-

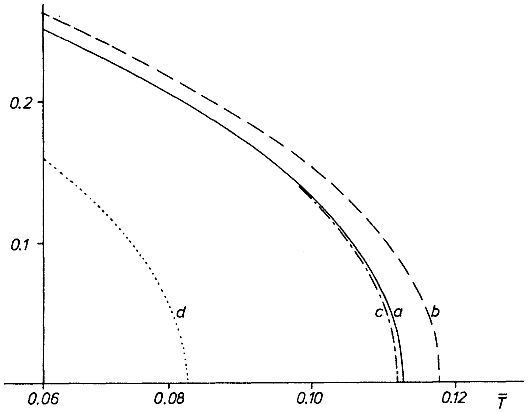

FIG. 2. Polarization curves of a defect crystal with different defect site correlations. Dimensionless quantities $\bar{A}=-A/J$, $\bar{\Lambda}=-\Lambda/J$, $\bar{T}=Tk_BB/J^2$, and $\bar{x}=\sqrt{-B/J}x$ are introduced. Values of parameters are $\bar{A}=2.75$, $\Delta\bar{A}=-1$, $\bar{\Lambda}=0.75$, $\Delta\bar{B}=\epsilon=0$, $c^1=0.1$. The correlation K is 0, 0.04, and -0.01 for curves a,b, and c, respectively. (For comparison curve d shows the polarization following from a simple VC-type calculation.)

creasing correlations. For equal defect concentration, the polarization and T_c increase when going from repulsive over random to attractive defect distributions. In the case considered, the variation of T_c due to a change of the defect site correlations amounts to as much as about 5%. An investigation of different concentrations and different magnitudes of the defect potentials showed that the effect is larger for a crystal with a low concentration of strong defects than for a high concentration of weak defects. The ferroelectric properties are also effected by a variation of the symmetries of the interaction and of the correlation from cubic to tetragonal.[20]

In addition to these static quantities we determined the change of the dispersion curves with defect site correlations. The Fourier transform of the displacement-displacement correlation function,

$$S(\vec{k},\omega)=\sum_{\vec{m}}\int_{-\infty}^{\infty}dt\,e^{-i(\vec{k}\cdot\vec{m}-\omega t)}\times\langle u_{\vec{0}}(0)u_{\vec{m}}(t)\rangle\ , \tag{5.8}$$

can be calculated—making use of SCPA to obtain an effective harmonic Hamiltonian—from the respective Green's function G by means of the fluctuation-dissipation theorem (cf., for example, Ref. 3). For a crystal with defects one has to replace the classical statistical mechanics expression for a perfect crystal,

$$S(\vec{k},\omega)\sim\frac{1}{\omega}\mathrm{Im}G^R(\vec{k},\omega^2)\ , \tag{5.9}$$

with the retarded Green's function,

$$\mathrm{Im}G^R(\vec{k},\omega^2)=\lim_{\epsilon\to 0+}\mathrm{Im}G(\vec{k},\omega^2-i\epsilon)\ ,$$

by

$$\langle S(\vec{k},\omega)\rangle\sim\frac{1}{\omega}\mathrm{Im}\langle G^R(\vec{k},\omega^2)\rangle \tag{5.10}$$

From Eqs (2.9) and (3.11) one obtains the scattering function $\langle S(\vec{k},\omega)\rangle$ for defect crystals with correlated defect sites. For a one-dimensional crystal, for example, with NN interaction the potential [Eq. (5.7)] has the form

$$\Phi_{nm}=\delta_{nm}(\Phi+\Delta\Phi\tau_n^1)+J(\delta_{n,m+1}+\delta_{n,m-1})\ .$$

The dispersion of the perfect crystal is

$$\omega^2(k)=\Phi+2J\cos k,\quad k\in[-\pi,\pi]\ .$$

From Eq. (3.1) one has

$$V^1=-\Delta\Phi+c^1\Delta\Phi,\quad\text{and } V^2=c^1\Delta\Phi\ . \tag{5.11}$$

$\langle t^1\rangle$ and $\langle t^2\rangle$ may be calculated by means of Eq. (3.5) from the virtual-crystal Green's function,

$$P_{00}(\omega^2)=\left[\left[\frac{\Phi+c^1\Delta\Phi-\omega^2}{2J}\right]^2-1\right]^{-1/2}\kappa/2J\ ,$$

with $\kappa=1,-i,-1$ for $\Phi+c^1\Delta\Phi-\omega^2<2J$, $>2J$, and $<-2J$, $>-2J$, respectively. The self-energy $\Sigma(k)$ is then obtained from Eq. (3.11) by introducing the Fourier transforms of $P_{mn}^{\mu\nu}$ and P_{nm}. In the present example we consider only nearest-neighbor correlations which are given by the constant [cf. Eq. (3.4)]

$$K:=(c^1)^2k_{01}^{11}\ .$$

By means of the so-determined scattering function $\langle S(k,\omega)\rangle$ one may calculate dispersion curves for defect crystals and investigate the influence of the correlation K. For every k $\langle S(k,\omega)\rangle$ has sharp resonances for two frequencies which define two dispersions $\omega_1(k)$ and $\omega_2(k)$. These are represented in Fig. 3 for $\Delta\Phi=1$ (defect potential steeper) and different values of K. While the K dependence of the host band ω_2 is rather weak (order of magnitude is 1%, not visible in the figure), the correlation influence on the defect band ω_1 is very pronounced.

VI. SUMMARY AND DISCUSSION OF RESULTS

In the present paper methods were developed for a treatment of crystals with site-correlated defects in such a way that the virtual crystal or the CPA

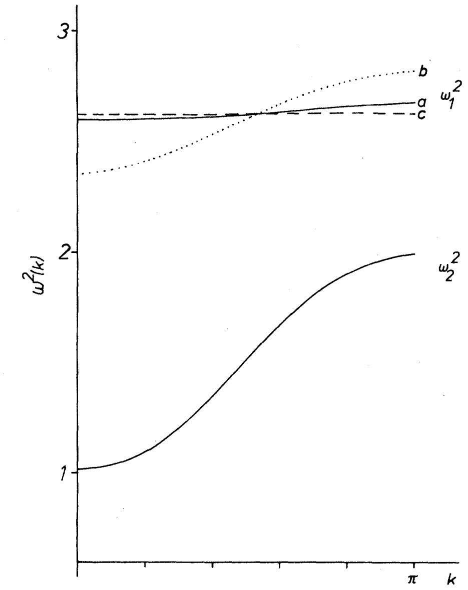

FIG. 3. Dispersion curves of a defect crystal with different defect site correlations. Values of parameters are $A=1.5$, $\Delta A=1$, $J=-0.25$, $c^1=0.1$. ω_1 and ω_2 are the defect-band and the host-band dispersions. The values of the correlation K are 0, 0.04, and -0.01 for curves a,b, and c, respectively.

crystal with no correlations was taken as reference system. As a consequence there are now two types of defects and four interconnected correlation functions and the expression for the $\vec{k}$- and ω-dependent self-energy is changed from Eqs. (2.18) to (3.11). Owing to this alteration of the reference system the Green's function may now be calculated for all concentrations. The averaging procedure employed in this paper can be extended, without difficulty, to an arbitrary number of types of defects. It may be employed, therefore, to deal with solid solutions of more than two components. In this method arbitrary correlations may be prescribed. The larger their range, the more extended are the calculations.

The conditionally averaged Green's functions (which were calculated by averaging over those configurations only in which there is an atom of a given type at a certain lattice site) are the basis for an SCPA treatment of ferroelectrics with correlated defect sites.

The results show a strong influence of the correlation on the ferroelectric properties. Compared to a random distribution, an attractively correlated distribution increases the polarization and the critical temperature, while a repulsive correlation decreases P and T_c.[20,21] Both for VCA and CPA crystals with random defects as reference systems the general calculations described above were carried so far that the results are obtained in terms of integrals over the Brillouin zone and inverses of low-dimensional matrices. These can be calculated explicitly (numerically if necessary) for any special crystal.

The dispersion curves derived from the Green's function show a strong correlation dependence of the defect band (ω_1^2 in Fig. 3); its dispersion increases with increasingly attractive correlations. This remarkable influence of correlations can be illustrated with the help of a simple model. We consider the localized vibrations which arise since the frequency ω_1 is too large for the host crystal, so that no propagating phonons can occur, and discuss, in a one-dimensional model, the limiting cases $k=0$ and $k=\pi$.

$k=0$: (A) For repulsive correlations (dashed line in Fig. 3) the average distance between defects is large. $\omega_1(0)$ is then mainly determined by the mass of a single defect, its one-body potential, and its coupling to the rest of the crystal. It is relatively large. (B) For attractive correlations (dotted line in Fig. 3) the defects are clustered, e.g., in pairs. Such a pair is vibrating as a whole in the rest of the crystal. As compared to (A) the vibrating mass is now larger and, thus, the frequency smaller.

$k=\pi$: (A) The situation is now similar to case (A) for $k=0$. For, due to the smallness of the amplitude of the nearest-neighbor vibrations, the opposite sense of these vibrations leads only to a slight increase of the frequency. (B) Now the two atoms of a defect pair vibrate with opposite sense against each other. Owing to the NN interaction there is now an increased coupling constant leading to a marked rise of the frequency.

Correlations in solid solutions have been determined experimentally, e.g., by diffuse x-ray or neutron scattering.[22,23] Measurements of $\mathrm{Fe}_x\mathrm{Cr}_{1-x}$ with 6.5 at. % Fe (Ref. 24), e.g., yielded correlations of the same order of magnitude as those assumed above: Measured NN correlations were $K=0.02$, while the correlations presumed in this paper ranged from $K=-0.01$ to $K=0.04$.

The calculated correlation dependence (e.g., of the dispersion or polarization curves) can be tested by comparing specimens of the same material with different defect site correlations. Such specimens are produced if the crystals are grown by different procedures (e.g., from the melt and from solution). The actual correlations could then be determined by diffuse scattering experiments and the dispersion by inelastic scattering.

ACKNOWLEDGMENT

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APPENDIX: DERIVATION OF EQ. (4.1) FROM EQ. (4.9) FOR VANISHING CORRELATIONS

For defects distributed at random, i.e., for $\underline{P}'=\underline{P}-P_{\vec{0}\vec{0}}\underline{\mathbb{1}}$, we prove the auxiliary equations

$$V-\Sigma=(1+\langle t\rangle P_{\vec{0}\vec{0}})^{-1}(t-\langle t\rangle)(1+P_{\vec{0}\vec{0}}t)^{-1}\,, \tag{A1a}$$

$$t-\langle t\rangle=(1+\langle t\rangle P_{\vec{0}\vec{0}})(V-\Sigma)(1+P_{\vec{0}\vec{0}}t)\,, \tag{A1b}$$

$$\underline{PR}=\langle\underline{G}\rangle(\underline{\mathbb{1}}+\langle t\rangle P_{\vec{0}\vec{0}}\underline{\mathbb{1}})^{-1}\,, \tag{A2}$$

$$\underline{LP}=(\underline{\mathbb{1}}+\langle t\rangle P_{\vec{0}\vec{0}}\underline{\mathbb{1}})^{-1}\langle\underline{G}\rangle\,, \tag{A3}$$

$$\underline{A}=(1+P_{\vec{0}\vec{0}}\underline{\mathbb{1}}\langle t\rangle)^{-1}\langle\underline{G}\rangle(\underline{\mathbb{1}}+\langle t\rangle P_{\vec{0}\vec{0}}\underline{\mathbb{1}})^{-1}-P_{\vec{0}\vec{0}}(\underline{\mathbb{1}}+\langle t\rangle P_{\vec{0}\vec{0}}\underline{\mathbb{1}})^{-1}\,. \tag{A4}$$

Since, in the vector space X_Z, $P_{\vec{0}\vec{0}}$, t, $\langle t\rangle$, V, and Σ are matrices, we have to pay attention to the order of multiplications. Equations (A1) follow from Eq. (2.11) and the one-particle T matrix by insertion. Equation (A2) is proved by multiplying the relation

$$\langle\underline{G}\rangle=\underline{P}+\underline{P}(\underline{\mathbb{1}}-\langle t\rangle\underline{P}+\langle t\rangle P_{\vec{0}\vec{0}}\underline{\mathbb{1}})^{-1}\langle t\rangle\underline{P}\,,$$

from the right by $(\underline{\mathbb{1}}+\langle t\rangle P_{\vec{0}\vec{0}}\underline{\mathbb{1}})^{-1}$ and factoring out the expression $\underline{P}(\underline{\mathbb{1}}-\langle t\rangle\underline{P}+\langle t\rangle P_{\vec{0}\vec{0}}\underline{\mathbb{1}})^{-1}$. One thus obtains

$$\begin{aligned}\langle\underline{G}\rangle(\underline{\mathbb{1}}+\langle t\rangle P_{\vec{0}\vec{0}}\underline{\mathbb{1}})^{-1}&=\underline{P}(\underline{\mathbb{1}}-\langle t\rangle\underline{P}+\langle t\rangle P_{\vec{0}\vec{0}}\underline{\mathbb{1}})^{-1}[(\underline{\mathbb{1}}-\langle t\rangle\underline{P}+\langle t\rangle P_{\vec{0}\vec{0}}\underline{\mathbb{1}})+\langle t\rangle\underline{P}]\\&\quad\times(\underline{\mathbb{1}}+\langle t\rangle P_{\vec{0}\vec{0}}\underline{\mathbb{1}})^{-1}\\&=\underline{P}(\underline{\mathbb{1}}-\langle t\rangle\underline{P}+\langle t\rangle P_{\vec{0}\vec{0}}\underline{\mathbb{1}})^{-1}\,.\end{aligned}$$

Equation (A2) then follows from the definition of $\underline{R}$, Eq. (A3) is proved in an analogous way, and Eq. (A4) is proved by making use of Eq. (A3) as follows:

$$\begin{aligned}&(\underline{\mathbb{1}}+P_{\vec{0}\vec{0}}\underline{\mathbb{1}}\langle t\rangle)^{-1}\langle\underline{G}\rangle(\underline{\mathbb{1}}+\langle t\rangle\underline{\mathbb{1}}P_{\vec{0}\vec{0}})^{-1}-P_{\vec{0}\vec{0}}(\underline{\mathbb{1}}+\langle t\rangle P_{\vec{0}\vec{0}}\underline{\mathbb{1}})^{-1}\\&\quad=(\underline{\mathbb{1}}-\underline{P}\langle t\rangle+P_{\vec{0}\vec{0}}\underline{\mathbb{1}}\langle t\rangle)^{-1}\underline{P}(\underline{\mathbb{1}}+\langle t\rangle P_{\vec{0}\vec{0}}\underline{\mathbb{1}})^{-1}-P_{\vec{0}\vec{0}}(\underline{\mathbb{1}}+\langle t\rangle P_{\vec{0}\vec{0}}\underline{\mathbb{1}})^{-1}\\&\quad=(\underline{\mathbb{1}}-\underline{P}\langle t\rangle+P_{\vec{0}\vec{0}}\underline{\mathbb{1}}\langle t\rangle)^{-1}[\underline{P}-(\underline{\mathbb{1}}-\underline{P}\langle t\rangle+P_{\vec{0}\vec{0}}\underline{\mathbb{1}}\langle t\rangle)P_{\vec{0}\vec{0}}](\underline{\mathbb{1}}+\langle t\rangle P_{\vec{0}\vec{0}}\underline{\mathbb{1}})^{-1}\\&\quad=(\underline{\mathbb{1}}-\underline{P}\langle t\rangle+P_{\vec{0}\vec{0}}\underline{\mathbb{1}}\langle t\rangle)^{-1}[(\underline{P}-P_{\vec{0}\vec{0}}\underline{\mathbb{1}})(1+\langle t\rangle P_{\vec{0}\vec{0}})](\underline{\mathbb{1}}+\langle t\rangle P_{\vec{0}\vec{0}}\underline{\mathbb{1}})^{-1}\\&\quad=(\underline{\mathbb{1}}-\underline{P}\langle t\rangle+P_{\vec{0}\vec{0}}\underline{\mathbb{1}}\langle t\rangle)^{-1}(\underline{P}-P_{\vec{0}\vec{0}}\underline{\mathbb{1}})\,.\end{aligned}$$

These auxiliary equations are then used to obtain the desired results: Introducing Eqs. (A1b)–(A4) into Eq. (4.9) one has

$$\begin{aligned}\langle\Gamma^{\vec{i}}_{\vec{m}\vec{n}}\rangle=\langle G_{\vec{m}\vec{n}}\rangle+\langle G_{\vec{m}\vec{i}}\rangle&(1+\langle t\rangle P_{\vec{0}\vec{0}})^{-1}[(1+\langle t\rangle P_{\vec{0}\vec{0}}(V-\Sigma)(1+P_{\vec{0}\vec{0}}t)]\\&\times[1-(1+P_{\vec{0}\vec{0}}\langle t\rangle)^{-1}\langle G_{\vec{0}\vec{0}}\rangle(1+\langle t\rangle P_{\vec{0}\vec{0}})^{-1}(1+\langle t\rangle P_{\vec{0}\vec{0}})\\&\quad\times(V-\Sigma)(1+P_{\vec{0}\vec{0}}t)-P_{\vec{0}\vec{0}}(1+\langle t\rangle P_{\vec{0}\vec{0}})^{-1}(1+\langle t\rangle P_{\vec{0}\vec{0}})(V-\Sigma)\\&\quad\times(1+P_{\vec{0}\vec{0}}t)]^{-1}(1+P_{\vec{0}\vec{0}}\langle t\rangle)^{-1}\langle G_{\vec{i}\vec{n}}\rangle\,.\end{aligned}$$

Reducing by $(1+\langle t\rangle P_{\vec{0}\vec{0}})$ and $(1+P_{\vec{0}\vec{0}}t)$ one obtains

$$\langle \Gamma^{\vec{i}}_{\vec{m}\,\vec{n}} \rangle = \langle G_{\vec{m}\,\vec{n}} \rangle + \langle G_{\vec{m}\,\vec{i}} \rangle (V-\Sigma) [(1+P_{\vec{0}\,\vec{0}} \langle t \rangle)(1+P_{\vec{0}\,\vec{0}} t)^{-1} + (1+P_{\vec{0}\,\vec{0}} \langle t \rangle) P_{\vec{0}\,\vec{0}} (V-\Sigma) - \langle G_{\vec{0}\,\vec{0}} \rangle (V-\Sigma)]^{-1} \langle G_{\vec{i}\,\vec{n}} \rangle \, .$$

Making use of Eq. (A1a) then leads to Eq. (4.1).

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