On the Computation of Lattice Green's Functions by Sine Series Expansions

O. RA

Institute of Physical Chemistry, Technical University of Norway, Trondheim

(Z. Naturforsch. **26 a**, 111—123 [1971]; received 6 November 1970)

Mahanty has pointed out that by expanding the imaginary part of a lattice Green's function in a sine series, direct numerical treatment of the principal value integral which determines the real part of a Green's function of real argument can be circumvented. Here Mahanty's result is extended to cover Green's functions of purely imaginary arguments. Also, alternative expressions which, in certain cases, simplify numerical computations are recorded. Whereas the aforementioned formulas are of quite general validity, an included recurrence relation, which links defect induced changes in moments of the frequency distribution with the Fourier coefficients, is restricted to the case of a mass defect in a diagonally cubic lattice. The prospects of applying Mahanty's method to moderately complex polyatomic crystals are assessed on the basis of computations pertaining to alkaline earth fluorides. It is found, through studying simple point defects in CaF_2, SrF_2, and BaF_2, that by truncating the sine series expansions when associated functionals assume satisfactory values at functions which are constants on the set of phonon frequencies, one obtains sets of Fourier coefficients containing sufficient information to cover a variety of defect properties. Also the number of Fourier coefficients is no larger than to preserve a chief merit of the method, namely the provision of a convenient way of condensing and storing information. For the type of lattices considered Mahanty's way of evaluating Fourier coefficients is found to be impracticable. However, upon supplementing the sine series expansion method by an adaptation of Gilat's extrapolation procedure for frequency spectra, Brillouin zone integrations involving rapidly varying functions become redundant.

1. Introduction

The feasibility of a theoretical attack on effects conditioned by the vibrational behaviour of imperfect crystals in many cases depends largely on an efficient generation of lattice Green's functions (GF). To facilitate the numerical construction of such functions Mahanty has recommended that imaginary parts of GF's be represented by sine series expansions[1]. It is our aim in this paper to examine the prospects of applying this method to more complex crystals than the monoatomic lattices considered by Mahanty and coworkers. Work in this direction seems warranted since it is not a priori clear that the convergence properties of "polyatomic" sine series approximations are such as to render expedient Mahanty's original formulation. By way of illustration we present calculations on GF's for the alkaline earth fluorides CaF_2, SrF_2, and BaF_2. However, before turning to these results we outline briefly the crux of the sine series expansion method while adding some, in the author's opinion useful, relations to the ones already reported by Mahanty.

2. Theory

Mahanty relates his treatment to Brillouin zone (BZ) integrals from the outset. For reasons to become apparent shortly we shall proceed in a somewhat different manner. Consider the by now well known expansion[2]

$$G_0(l\varkappa\alpha, l'\varkappa'\beta;\omega) = N^{-1}(M_{0\varkappa}M_{0\varkappa'})^{-1/2}\sum_{\boldsymbol{k}j} R(l\varkappa\alpha, l'\varkappa'\beta;\boldsymbol{k}j)(\omega^2-\omega_{\boldsymbol{k}j}^2)^{-1},$$

$$R(l\varkappa\alpha, l'\varkappa'\beta;\boldsymbol{k}j) = e_\alpha(\varkappa|\boldsymbol{k}j)\,e_\beta^*(\varkappa'|\boldsymbol{k}j)\exp[i\boldsymbol{k}\cdot\{\boldsymbol{x}(l\varkappa)-\boldsymbol{x}(l'\varkappa')\}] \quad (1$$

of a perfect lattice displacement-displacement Green's function. The various symbols appearing in the above expression have their usual significance. Upon Im $\omega \to O^+$ the real and imaginary parts of $G_0(l\varkappa\alpha, l'\varkappa'\beta;\omega)$ approach limits connected by a dispersion relation, viz.

$$\mathrm{Re}\,G_0(l\varkappa\alpha, l'\varkappa'\beta;\omega+iO) = \pi^{-1}\mathscr{P}\int_{-\infty}^{\infty}\mathrm{Im}\,G_0(l\varkappa\alpha, l'\varkappa'\beta;\omega'+iO)(\omega'-\omega)^{-1}\,\mathrm{d}\omega' \quad (2$$

[1] J. MAHANTY, Proc. Phys. Soc. London 88, 1011 [1966]. [2] A. A. MARADUDIN, Rep. Progr. Phys. 28, 331 [1965].

which equation is a consequence of the analyticity of the retarded Green's function in the upper-half complex plane[3]. For computational purposes it is convenient to consider ω^2 rather than ω to be the argument of immediate interest. Letting B denote the finite union of intervals coinciding with $\{\overline{\omega^2_{kj}}\}$ in the large N limit, setting $\omega^2_L = \sup\{\omega^2 : \omega^2 \in B\}$, and making use of the fact that $\operatorname{Im} G_0(l\varkappa\alpha, l'\varkappa'\beta; \omega^2 + iO) = 0$ for $\omega^2 \in \tilde{B}$, one has

$$\operatorname{Re} G_0(l\varkappa\alpha, l'\varkappa'\beta; \omega_L^2 x + iO) = \pi^{-1}\mathscr{P}\int_0^1 \operatorname{Im} G_0(l\varkappa\alpha, l'\varkappa'\beta; \omega_L^2 x' + iO)\,(x' - x)^{-1}\,dx' \tag{3}$$

where $x = \omega^2/\omega_L^2$. Furthermore, the distributional relation $(x \pm iO)^{-1} = \mp i\pi\delta(x) + \mathscr{P}x^{-1}$ in conjunction with Eq. (1) enables us to write

$$\operatorname{Im} G_0(l\varkappa\alpha, l'\varkappa'\beta; \omega_L^2 x + iO) = -\pi N^{-1}(M_{0\varkappa} M_{0\varkappa'})^{-1/2}\,\omega_L^{-2} \sum_{kj} R(l\varkappa\alpha, l'\varkappa'\beta; \boldsymbol{k}j)\,\delta(x - x_{kj}). \tag{4}$$

Given a test function $\Phi(x)$ whose support lies entirely within $(0, 1)$ and the sequence $\{s^p_{kj}(x)\}$ with $s^p_{kj}(x) = 2\sum_{n=1}^{p} \sin(n\pi x)\sin(n\pi x_{kj})$, then since[4].

$$\lim_{p\to\infty} \langle s^p_{kj}(x),\ \Phi(x)\rangle = \langle \delta(x - x_{kj}),\ \Phi(x)\rangle = \Phi(x_{kj})$$

we have

$$\operatorname{Im} G_0(l\varkappa\alpha, l'\varkappa'\beta; \omega_L^2 x + iO) = -2\pi N^{-1}(M_{0\varkappa} M_{0\varkappa'})^{-1/2}\,\omega_L^{-2} \sum_{kj} R(l\varkappa\alpha, l'\varkappa'\beta; \boldsymbol{k}j) \times \sum_{n=1}^{\infty} \sin(n\pi x)\sin(n\pi x_{kj}). \tag{5}$$

To obtain a convenient rearrangement of Eq. (5) we note that for an arbitrary $\varepsilon > 0$

$$\Big|\sum_{kj} \operatorname{Re}[R(l\varkappa\alpha, l'\varkappa'\beta; \boldsymbol{k}j)]\,\Phi(x_{kj}) - 2\sum_{n=1}^{m}\langle\{\sum_{kj} \operatorname{Re}[R(l\varkappa\alpha, l'\varkappa'\beta; \boldsymbol{k}j)]\sin(n\pi x_{kj})\} \times \sin(n\pi x), \Phi(x)\rangle\Big| \leqq \sum_{kj} \big|\operatorname{Re}[R(l\varkappa\alpha, l'\varkappa'\beta; \boldsymbol{k}j)]\{\Phi(x_{kj}) - \langle s^m_{kj}(x), \Phi(x)\rangle\}\big| \leqq \varepsilon$$

provided that

$m \geqq \max\{m_{kj}\}$ where m_{kj} is an integer with the property that

$|\Phi(x_{kj}) - \langle s^p_{kj}(x), \Phi(x)\rangle| \leqq \varepsilon\{\nu N\,|\operatorname{Re}[R(l\varkappa\alpha, l'\varkappa'\beta; \boldsymbol{k}j)]|\}^{-1}$ if $p > m_{kj}$

and ν is the number of atoms in a unit cell,

whence follows *

$$\operatorname{Im} G_0(l\varkappa\alpha, l'\varkappa'\beta; \omega_L^2 x + iO) = (M_{0\varkappa} M_{0\varkappa'})^{-1/2}\,\omega_L^{-2} \sum_{n=1} a_n(l\varkappa\alpha, l'\varkappa'\beta)\sin(n\pi x),$$

$$a_n(l\varkappa\alpha, l'\varkappa'\beta) = -2\pi N^{-1} \sum_{kj} R(l\varkappa\alpha, l'\varkappa'\beta; \boldsymbol{k}j)\sin(n\pi x_{kj}). \tag{6}$$

Moreover since [5]

$$\cos(x) = \pi^{-1}\mathscr{P}\int_{-\infty}^{\infty} \sin(x')\,(x' - x)^{-1}\,dx' = \pi^{-1}\int_{-\infty}^{\infty}\{\sin(x') - \sin(x)\}\,(x' - x)^{-1}\,dx'.$$

[3] D. N. Zubarev, Sov. Phys. Uspekhi **3**, 320 [1960].

[4] L. Schwartz, Mathematics for the Physical Sciences, Hermann, Paris 1966.

* Strictly speaking, the right hand sides of Eqs. (4,5) are generalized functions whatever the value of N, while the right hand side of Eq. (6) defines a locally integrable function in the large N limit. The three being equal on the open interval of interest, (0,1), we shall pay no distinction to this conceptual difference and refer to all three as $\operatorname{Im}_0 G(l\varkappa\alpha, l'\varkappa'\beta; \omega_L^2 x + iO)$.

[5] P. M. Morse and H. Feshbach, Methods of Theoretical Physics, McGraw-Hill, New York 1953.

Eq. (3) now reads

$$\begin{aligned}\operatorname{Re} G_0(l\varkappa\alpha, l'\varkappa'\beta; \omega_L^2 x + iO) = (M_{0\varkappa} M_{0\varkappa'})^{-1/2} \omega_L^{-2} \pi^{-1} \sum_{n=1} a_n(l\varkappa\alpha, l'\varkappa'\beta) \\ \times [\cos(n\pi x)\{\mathrm{Si}(n\pi x) + \operatorname{sgn}(1-x)\,\mathrm{Si}(n\pi|1-x|)\} \\ -\sin(n\pi x)\{\mathrm{Ci}(n\pi x) - \mathrm{Ci}(n\pi|1-x|)\}]\end{aligned} \tag{7a}$$

which expression is merely a compaction of Mahanty's Eq. (6) pertaining to in band functions and his remarks on the appropriate interpretation of $\mathrm{Si}(x)$ and $\mathrm{Ci}(x)$ for negative arguments. With calculations on defect induced changes in thermodynamic state functions in mind it seems desirable to extend this formula to cover also Green's functions of purely imaginary arguments. We therefore set $\omega = \pm i\omega_L\sqrt{y}$ and lift the $\mathscr{P}$ restriction to obtain

$$\begin{aligned}G_0(l\varkappa\alpha, l'\varkappa'\beta; -\omega_L^2 y) = (M_{0\varkappa} M_{0\varkappa'})^{-1/2} \omega_L^{-2} \pi^{-1} \sum_{n=1} a_n(l\varkappa\alpha, l'\varkappa'\beta) \\ \times [\cos(n\pi y)\{\mathrm{Si}(n\pi[1+y]) - \mathrm{Si}(n\pi y)\} - \sin(n\pi y)\{\mathrm{Ci}(n\pi[1+y]) \\ - \mathrm{Ci}(n\pi y)\}], \quad y \varepsilon \boldsymbol{R}^+.\end{aligned} \tag{7b}$$

For computational purposes, and even for certain formal arguments, it is convenient to express the sine and cosine integrals as

$$\mathrm{Si}(z) = \pi/2 - f(z)\cos(z) - h(z)\sin(z), \qquad \mathrm{Ci}(z) = f(z)\sin(z) - h(z)\cos(z), \tag{8}$$

$$f(z) = \int_0^\infty \mathrm{d}t \exp(-zt)/(t^2+1) = \int_0^\infty \mathrm{d}t \sin(t)/(t+z), \qquad h(z) = \int_0^\infty \mathrm{d}t \exp(-zt)\,t/(t^2+1) = \int_0^\infty \mathrm{d}t \cos(t)/(t+z),$$

whereupon Eqs. (7a, b) can be simplified to read

$$\begin{aligned}\operatorname{Re} G_0(l\varkappa\alpha, l'\varkappa'\beta; \omega_L^2 x + iO) = (M_{0\varkappa} M_{0\varkappa'})^{-1/2} \omega_L^{-2} \pi^{-1} \sum_{n=1} a_n(l\varkappa\alpha, l'\varkappa'\beta) \\ \times [\pi\cos(n\pi x) - f(n\pi x) + (-1)^{n+1} f(n\pi[1-x])], \quad x < 1,\end{aligned} \tag{9a}$$

$$\begin{aligned}G_0(l\varkappa\alpha, l'\varkappa'\beta; \omega_L^2 x) = (M_{0\varkappa} M_{0\varkappa'})^{-1/2} \omega_L^{-2} \pi^{-1} \sum_{n=1} a_n(l\varkappa\alpha, l'\varkappa'\beta) \\ \times [-f(n\pi x) + (-1)^n f(n\pi[x-1])], \quad x > 1,\end{aligned} \tag{9b}$$

$$\begin{aligned}G_0(l\varkappa\alpha, l'\varkappa'\beta; -\omega_L^2 y) = (M_{0\varkappa} M_{0\varkappa'})^{-1/2} \omega_L^{-2} \pi^{-1} \sum_{n=1} a_n(l\varkappa\alpha, l'\varkappa'\beta) \\ \times [f(n\pi y) + (-1)^{n+1} f(n\pi[y+1])], \quad y \in \boldsymbol{R}^+.\end{aligned} \tag{9c}$$

On the practical level the existence of a simple rational approximation to $f(z)$ for $z > 1$ (s.[6]) makes Eqs. (9a, b, c) become useful supplements to Eq. (7b) and to Mahanty's result Eq. (7a). Since the equivalence Eq. (7) $\Leftrightarrow$ Eq. (9) stems from a term by term equality, and since $\mathrm{Si}(z)$ and $\mathrm{Ci}(z) - \ln z$ can be represented by series expansions which converge rapidly for small z[6], the choice of the appropriate expression for a summand in the $0 < x < 1 + \pi^{-1}$ and $0 < y < \pi^{-1}$ cases depends on the value of n and on x or y. However, in the interests of speed and accuracy we recommend exclusive use of Eq. (9b, c) type summands when computing GF's corresponding to $x > 1 + \pi^{-1}$ or $y > \pi^{-1}$.

In § 4 we shall refer to the following expression for the change in Helmholz free energy accompanying the introduction of a mass defect,

$$M_{0\varkappa} \to M(l\varkappa) = M_{0\varkappa}[1 - \chi(l\varkappa)],$$

(the value attributed to l being immaterial), into a diagonally cubic lattice

$$\begin{aligned}\Delta\Omega = (3/2)\,kT \sum_{n=-\infty}^{\infty} (\ln\{[1 + \omega_n^2 M_{0\varkappa}\chi(l\varkappa) G_0(l\varkappa\alpha, l\varkappa\alpha; -\omega_n^2)][1-\chi(l\varkappa)]^{-1}\} \\ - N\Delta\mu_2[\omega_n^2 + \tfrac{1}{2}(\Delta\mu_4/\Delta\mu_2)]^{-1}) \\ + 3N\Delta\mu_2 \hbar \coth\{\tfrac{1}{2}\hbar(\tfrac{1}{2}\Delta\mu_4/\Delta\mu_2)^{1/2}/kT\}/\{4(\tfrac{1}{2}\Delta\mu_4/\Delta\mu_2)^{1/2}\},\end{aligned} \tag{10}$$

with $\omega_n = 2\pi n kT/\hbar$ and $\Delta\mu_{2p} = (3N)^{-1} \sum_r (\omega_r^{2p} - \omega_{0r}^{2p})$; $\{\omega_{0r}\} \equiv \{\omega_{\boldsymbol{k}j}\}$,

[6] M. Abramowitz and I. A. Segun, Handbook of Mathematical Tables, Dover, New York 1965.

and ω_r being a defective lattice frequency value. Eq. (10) constitutes an isolated mass defect restriction of a relation first obtained by MARADUDIN[7] from an infinite product representation of $\sin h\,(x)$ and recently rederived by the present author[8] from a graphical treatment of an infinite order perturbation expansion. For reasons to become clear in due course it is profitable to have access to the $\Delta\mu_{2p}$'s above without having to rely on the (squared) frequency distribution

$$F_{(0)}(\omega^2) = (3\varkappa N\pi)^{-1}\,\mathrm{Im}\,(\mathrm{d}/\mathrm{d}\omega^2)\ln|\boldsymbol{M}_{(0)}^{1/2}\boldsymbol{G}_{(0)}(\omega^2+iO)\,\boldsymbol{M}_{(0)}^{1/2}| \tag{11}$$

of the defective (perfect) lattice. (The above equation is Dyson's expression for the frequency spectrum[9] which, for later convenience, has been rewritten with recourse to the solutions of Heisenberg's equation of motion for harmonic lattice displacement-displacement GF's[10].)

By i) exploiting the moment-difference generating property of

$$(\mathrm{d}/\mathrm{d}\omega)\ln|\mathbf{1}-\boldsymbol{G}_0(\omega)\,\delta\boldsymbol{L}(\omega)|\ \ (\mathrm{s.}^{11}),\quad \text{where}\quad \delta\boldsymbol{L}(\omega)=\boldsymbol{G}_0(\omega)^{-1}-\boldsymbol{G}(\omega)^{-1},$$

ii) integrating by parts repeatedly to turn the integral representation Eq. (8) of $f(z)$ into an asymptotic expansion

$$f(z)\sim\sum_{p=0}^{(m)}(-1)^p(2p)!\,z^{-(2p+1)}\ \left(+(-1)^{m+1}(2m+2)!\int_0^\infty\frac{\sin(t)\,\mathrm{d}t}{[t+z]^{(2m+3)}}\right)$$

and similarly

$$f(z)'=-h(z)\sim\sum_{p=0}^{(m)}(-1)^{p+1}(2p+1)!\,z^{-(2p+2)}\ \left(+(-1)^m(2m+3)!\int_0^\infty\frac{\sin(t)\,\mathrm{d}t}{[t+z]^{(2m+4)}}\right),$$

iii) expanding terms $(x/[x-1])^m$ about "the point at infinity",

iv) and taking advantage of the fact that the coefficients of the asymptotic power series which results from dividing two asymptotic power series expansions may be obtained by formal substitution[12], explicit use of Eq. (11) can be circumvented. Instead, we find the following recurrence relation

$$[3N\Delta\mu_2\,\omega_{\mathrm{L}}^{-2}]=b_2[\chi(l\varkappa)-1]^{-1},$$

$$[3N\Delta\mu_{2p}\,\omega_{\mathrm{L}}^{-2p}]=[\chi(l\varkappa)-1]^{-1}\{b_{p+1}-\sum_{r=2}^{p}c_{p+1-r}[3N\Delta\mu_{2(r-1)}\,\omega_{\mathrm{L}}^{-2(r-1)}]\},\quad p\geqq 2 \tag{12}$$

where odd $m\Rightarrow$

$$b_m=6\chi(l\varkappa)(-1)^{(m-1)/2}(m-1)!\,\frac{(m-1)}{\pi^{m+1}}\sum_n{}'a_n(\varkappa)\,n^{-m}+3\chi(l\varkappa)\mathscr{C}_m(1),\ c_m=\chi(l\varkappa)\mathscr{D}_m$$

even $m\Rightarrow$

$$b_m=3\chi(l\varkappa)(-1)^{(m-2)/2}\frac{(m-2)!}{\pi^m}[1+m(m-2)]\sum_n(-1)^{n+1}a_n(\varkappa)\,n^{-(m-1)}+3\chi(l\varkappa)\mathscr{C}_m(2),$$

$$c_m=-\chi(l\varkappa)[\mathscr{E}_m-\mathscr{D}_m],$$

and

$$\mathscr{C}_m(i)=\sum_{p=0}^{2p+i<m}(-1)^p\frac{(2p)!}{\pi^{2p+2}}[2pm/(m-2p-1)+1]\binom{m-1}{2p+1}\sum_n(-1)^{n+1}a_n(\varkappa)\,n^{-(2p+1)},$$

$$\mathscr{D}_m=\sum_{p=0}^{2p<m}(-1)^{p+1}\frac{(2p)!}{\pi^{2p+2}}\binom{m}{m-2p}\sum_n(-1)^{n+1}a_n(\varkappa)\,n^{-(2p+1)},$$

$$\mathscr{E}_m=2(-1)^{m/2}\frac{m!}{\pi^{m+2}}\sum_n{}'a_n(\varkappa)\,n^{-(m+1)},\ a_n(\varkappa)=a_n(l\varkappa\alpha,l\varkappa\alpha),$$

[7] A. A. MARADUDIN, Phonons and Phonon Interactions, Benjamin, New York 1964.
[8] O. RA, Acta Chem. Scand., in press.
[9] F. J. DYSON, Phys. Rev. **92**, 1331 [1953].
[10] R. J. ELLIOT and D. W. TAYLOR, Proc. Phys. Soc. London **83**,189 [1964].
[11] A. A. MARADUDIN, E. W. MONTROLL and G. H. WEISS, Theory of Lattice Dynamics in the Harmonic Approximation, Academic, New York 1963.
[12] A. ERDELYI, Asymptotic Expansions, Dover, New York 1956.

and where a prime on a summation over n signifies that n is to assume odd values only. As a control we make use of Eq. (9) to derive the following asymptotic representation of the summands appearing in Eq. (10)

$$3\ln\{[1+\omega_n^2 M_{0\varkappa}\chi(l\varkappa)G_0(l\varkappa\alpha, l\varkappa\alpha; -\omega_n^2)][1-\chi(l\varkappa)]^{-1}\} - 3N\Delta\mu_2[\omega_n^2 + \tfrac{1}{2}(\Delta\mu_4/\Delta\mu_2)]^{-1} \sim \sum_{m=1}\gamma_m y_n^{-m}, \quad y_n \to \infty \tag{13}$$

where $y_n = (\omega_n/\omega_L)^2$ and where

$$\gamma_m = 3[\sum_{q=1}^{q\leq m}(-1)^{q+1}q^{-1}(1-\chi(l\varkappa))^{-q}\sum_{i=1}^{\mathscr{R}(m)}\prod_{s=1}^{q}\beta_{\boldsymbol{k}_s^{(i)}}] + (-1)^m(3N\Delta\mu_2/\omega_L^2)(\tfrac{1}{2}[\Delta\mu_4/\omega_L^4]/[\Delta\mu_2/\omega_L^2])^{(m-1)}.$$

$\mathscr{R}(m)$ is the number of ways of partitioning m into q non-zero integers, the i^{th} partition defining a set $\{k_s^{(i)};\ s=1,q\}$ with the property $\sum_s k_s^{(i)} = m$. $\{\beta_r\}$ is given by

$$r \text{ odd} \Rightarrow \beta_r = \chi(l\varkappa)(-1)^{r+1}\mathscr{D}_r, \qquad r \text{ even} \Rightarrow \beta_r = \chi(l\varkappa)[\mathscr{E}_r + (-1)^{r+1}\mathscr{D}_r].$$

Upon setting $m = 1, 2, 3$ with allowance for Eq. (12) it follows that $\gamma_1 = \gamma_2 = 0 \neq \gamma_3$, in consistency with the correct large y_n behaviour of the summands referred to[7]. In writing Eqs. (12), (13) we have utilized the relation

$$(-2/\pi^2)\sum_n{}' a_n(l\varkappa\alpha, l'\varkappa'\beta)n^{-1} = \delta_{ll'}\delta_{\varkappa\varkappa'}\delta_{\alpha\beta} \tag{14}$$

which is merely another way of expressing the closure conditions on the eigenvectors of the mass weighted perfect lattice force constant matrix in the site representation. The sum-rule Eq. (14), which went unmentioned by Mahanty, is of importance for proper renormalization of truncated sine series expansions before calculating correlation functions or quantities which depend critically on the limiting properties of GF's as $|\omega| \to \infty$.

3. The Lattice Model

The CaF_2, SrF_2, and BaF_2 polarization vectors and mode frequencies involved in calculations to receive attention in succeeding sections have been computed on a central force version of the shell model[13], both anions and cations being allowed to deform in the course of vibrations. The short — range part of interionic potentials was assumed to originate in shell — shell interactions, the corresponding force constants being taken from previously reported semiempirical "overlap-charge" calculations[14]. A discussion of shell parameters will appear elsewhere[15]. Suffice it here merely to remark that for all three crystals a set of parameter values could be found which brings the model into reasonable consistency with the experimental data available, the agreement in the three cases improving in the order: CaF_2, SrF_2, BaF_2. This statement should not be taken to imply that we believe a simple model of this kind to furnish a particularly realistic description of the actual state of affairs. As recently demonstrated by the author[14] even the drastic assumption that the three alkaline earth fluorides are of the ideally ionic type is incompatible with a central force model (and also with an "elaboration" based on the addition of so-called empirical non-central contributions to first and second neighbour interactions for that matter) since the non-orthogonality of (free) ion wave functions centred on the nuclei of both nearest and next nearest ion pairs gives rise to appreciable three-body forces of long range. However, a somewhat tenuous connection with the real force fields in CaF_2, SrF_2, and BaF_2 notwithstanding, the model does have the virtue of leading to computational simplicity; a mitigating feature which more often than not is being invoked in lattice dynamics calculations.

4. Numerical Calculations

In this section we describe a procedure currently being put to use in automatic computations of GF's for alkaline earth fluorides. Although the remarks to be encountered below relate to work on CaF_2, SrF_2, and BaF_2, this material presumably has suf-

[13] R. A. Cowley, Proc. Roy. Soc. London A **268**, 109 [1962].
[14] O. Ra, J. Chem. Phys. **52**, 3765 [1970].
[15] O. Ra, to be published.

ficient general bearing on moderately complex lattices to warrant its use for illustrational purposes.

Letting aside highly artificial lattice models the set $\{a_n(l\varkappa\alpha,\ l'\varkappa'\beta)\}$ cannot be obtained in closed form. However, with recourse to numerical methods one may still evaluate Fourier coefficients of this type by carrying out an integration over the first BZ. This possibility when advocated by Mahanty in his work previously cited had already been made use of by AGGARWAL et al. in a paper on density of states computations[16]. Another method, suggested by TEWARY[17], invokes a well known matrix theorem due to Born to circumvent the need for calculating eigenvectors and eigenvalues. Instead, a matrix power series has to be dealt with numerically. Unfortunately, neither method was found to be suitable in our case. No criticism intended, the matrix power series approach was shelved simply because polarization vectors and vibration frequencies were required anyway for other purposes, a need which is likely to arise in a lattice dynamics investigation. Also, after an unsuccessful attempt to construct an integration routine capable of coping efficiently with large-n coefficients the BZ integration method was abandoned. The difficulties experienced by the author were due mainly to the occurrence of very rapidly oscillating integrands. To the author's knowledge there is as yet no integration algorithm available which lends itself to a treatment of rapidly varying integrands without extensive sampling. That this lack did not pose any serious problem for AGGARWAL et al.[16] when calculating Fourier coefficients for frequency spectra of some cubic Bravais lattices is hardly surprising. First, the spectra in question can be approximated by comparatively few sine functions without severe loss of accuracy. As a result only well-behaved integrands come into play. Second, the diagonalization of the Fourier transformed dynamical matrix of a monoatomic model crystal based on short-range forces requires a modest numerical effort and can be readily effected for a large number of $\boldsymbol{k}$ values. This simplicity is not generally attained for polyatomic lattices being partly kept together by long-range coulomb forces. For CaF_2, SrF_2, and BaF_2 the $\boldsymbol{k}$ dependence exhibited by several of the frequency branches is such as to induce pronounced peaking of frequency spectra and GF's. The attendant necessity of retaining a relatively large number of terms in the sine series leads to integrands which are markedly less well-behaved than the ones encountered by AGGARWAL et al.[16]. Even the admittedly crude lattice model commented upon above would call for an appreciable amount of computer time if the coupled core-shell matrix equations were to be constructed and solved for an extremely fine mesh of sampling points in the irreducible part of $\boldsymbol{k}$-space. Altogether, it was found advantageous to replace the BZ integrations with an adaptation of the extrapolation method devised by GILAT and collaborators[18–20] for frequency spectra. Upon

---

i) writing

$$\operatorname{Im} G_0(l\varkappa\alpha,\ l'\varkappa'\beta;\ \omega_L^2 x + iO) = -\pi (M_{0\varkappa} M_{0\varkappa'})^{-1/2}\, \omega_L^{-2} \sum_j \lim_{\Delta x \to 0} \left([\operatorname{mes}(E_j)^{-1} \right. \tag{15}$$

$$\left. \times \int_{E_j} S(l\varkappa\alpha,\ l'\varkappa'\beta;\ \boldsymbol{k}j)\, \mathrm{d}\boldsymbol{k}\right] \lim_{N\to\infty} \left[\left\langle \sum_{\boldsymbol{k}} \delta(z - x_{\boldsymbol{k}j}),\ \psi_{(x,x+\Delta x)}(z)\right\rangle / (N\,\Delta x)\right]),$$

$$E_j = \{\boldsymbol{k}:\ x_{\boldsymbol{k}j} \in (x, x+\Delta x)\}, \qquad \psi_{(x,x+\Delta x)}(z) = 1 \quad \text{if} \quad z \in (x, x+\Delta x) \quad \text{and 0 otherwise},$$

$$S(l\varkappa\alpha,\ l'\varkappa'\beta;\ \boldsymbol{k}j) = r(\boldsymbol{k})\, h(\boldsymbol{k})^{-1} \sum_{\boldsymbol{k}' \in \boldsymbol{k}^* \cup (-\boldsymbol{k})^*} R(l\varkappa\alpha,\ l'\varkappa'\beta;\ \boldsymbol{k}'j);$$

with $\boldsymbol{k}^*$ denoting the star of $\boldsymbol{k}$ comprising $h(\boldsymbol{k})$ members, and with $r(\boldsymbol{k}) = 1$ if $-\boldsymbol{k} \in \boldsymbol{k}^*$ (as is the case for a fluorite type crystal) and $\frac{1}{2}$ otherwise. [There can be no doubt that Eq. (15) is compatible with Eq. (6). By construction, the large N limit of the right hand side of Eq. (6) converges to the right hand side of Eq. (15) in the mean square sense. In addition, by virtue of Carleson's recent result[21] the right hand side of Eq. (6) converges pointwise to that of Eq. (15) almost everywhere.]

---

[16] K. G. AGGARWAL, J. MAHANTY, and V. K. TEWARY, Proc. Phys. Soc. London **86**, 1225 [1965].
[17] V. K. TEWARY, Proc. Phys. Soc. London **92**, 987 [1967].
[18] G. GILAT and G. DOLLING, Phys. Letters **8**, 304 [1964].
[19] G. GILAT and L. J. RAUBENHEIMER, Phys. Rev. **144**, 390 [1966].
[20] L. J. RAUBENHEIMER and G. GILAT, Phys. Rev. **157**, 586 [1967].
[21] L. CARLESON, Acta Math. **116**, 135 [1966].

ii) assuming that all singularities are contained in a finite set of isolated critical points. (This assumption, which in addition to being plausible is also reinforced by experience, makes

$$\operatorname{Im} G_0(l\varkappa\alpha, l'\varkappa'\beta;\, \omega_L^2 x + iO)$$

become a bounded and continuous function of bounded variation, which, in turn, makes the right hand side of Eq. (6) converge uniformly to that of Eq. (15) over all intervals contained in $\omega_L^{-2} B$.)

iii) assuming

$$S(l\varkappa\alpha, l'\varkappa'\beta;\, \boldsymbol{k}^c j) + \operatorname{grad} S(l\varkappa\alpha, l'\varkappa'\beta;\, (\boldsymbol{k} = \boldsymbol{k}^c) j) \cdot (\boldsymbol{k} - \boldsymbol{k}^c)$$

to represent $S(l\varkappa\alpha, l'\varkappa'\beta;\, \boldsymbol{k} j)$ with reasonable accuracy throughout a small cube centred at $\boldsymbol{k}^c$,

the required modification of the extrapolation method merely amounts to multiplying the volume of a layer confined by closely spaced constant-frequency surfaces by a layer average of $S(l\varkappa\alpha, l'\varkappa'\beta;\, \boldsymbol{k} j)$, the mean value being calculated from the above linear expression. Given a practically continuous numerical representation of $\operatorname{Im} G_0(l\varkappa\alpha, l'\varkappa'\beta;\, \omega_L^2 x + iO)$ it is trivial to calculate Fourier coefficients

$$\{a_n(l\varkappa\alpha, l'\varkappa'\beta);\, n \leqq N_a\}$$

for (almost) arbitrary N_a.

The validity of computing S values on the basis of linear extrapolation was tested for various layers by actually diagonalizing the CaF_2 dynamical matrix at all $\boldsymbol{k}$-values involved in the averaging procedure. Sufficiently good agreement was obtained in all cases. For all three crystals the 9×9 effective dynamical matrix

$$\boldsymbol{C}(\boldsymbol{k})^{\mathrm{eff}} = \boldsymbol{M}_0^{-1/2} \{\boldsymbol{C}(\boldsymbol{k})^{\mathrm{cc}} - \boldsymbol{C}(\boldsymbol{k})^{\mathrm{cs}} \boldsymbol{C}(\boldsymbol{k})^{\mathrm{ss}^{-1}} \boldsymbol{C}(\boldsymbol{k})^{\mathrm{sc}}\} \boldsymbol{M}_0^{-1/2}$$

(cc referring to core-core couplings etc.) has been diagonalized at points $\{\boldsymbol{k}^c\}$ and

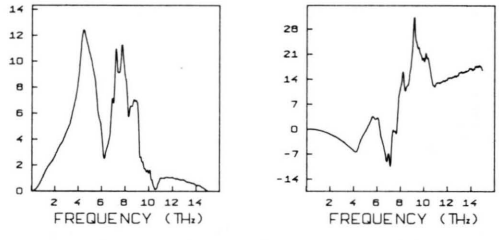
$$\{\boldsymbol{k}^c + \Delta \boldsymbol{k}_i^c \;\; (i = 1, 3)\},$$

where $\{\boldsymbol{k}^c\}$ forms a uniform mesh over most of the unique portion of the first BZ. In remaining regions, which are neighbourhoods of $\boldsymbol{k}$ values associated with critical points in the density of states, a finer mesh was applied. For each lattice the total number of $\boldsymbol{C}(\boldsymbol{k})^{\mathrm{eff}}$-diagonalizations was ~ 4800, which number includes also complete diagonalizations at points $\boldsymbol{k}^c + \Delta \boldsymbol{k}_i^c$. The latter diagonalizations, replacing thus the first order perturbation scheme used by GILAT et al.[18–20], were performed to insure reliable estimates of grad S**. To test the programming work and to probe the reliability of a Houston type scheme described by the author in a previous paper[22], out of band GF's for CaF_2 were computed from Eq. (9b), by the Houston type approach, and also by a direct summation over a b.c.c. grid of wave vectors corresponding to a direct lattice of 64000 cells. Satisfactory agreement was obtained at the ω^2 values investigated.

Extensive tabulations of $a_n(l\varkappa\alpha, l'\varkappa'\beta)$ values for the core-core, core-shell, and shell-shell GF's of the three crystals have been prepared and will be made available in a forthcoming paper. Since a scrutiny of convergence rates of sine function expansions for core-shell, shell-shell, and off-diagonal core-core GF's did not add substantially to the information on convergence properties obtainable from diagonal core-core GF's, a discussion of the latter functions and derived quantities will suffice here. The approximations to diagonal GF's shown in Figs. 1—6 represent the result of projecting numerically given functions on a finite dimensional subspace

$$\{\sin(n\pi x),\; n = 1,\; N_a(= 149)\};$$

the Fourier coefficients having been obtained by repeated application of Simpson's one-third rule over subintervals the common length of which was



1 a 1 b

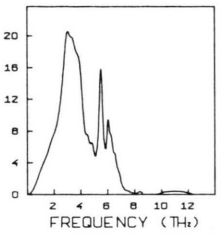
Fig. 1a. — $\omega_L^2 M_{01} \operatorname{Im} G_0(l1\alpha, l1\alpha;\, \omega_L^2 x + iO)$ for Ca^{2+} in CaF_2; $\alpha = x, y,$ or z.

Fig. 1b. $\omega^2 M_{01} \operatorname{Re} G_0(l1\alpha, l1\alpha;\, \omega_L^2 x + iO) \cdot 10$ for Ca^{2+} in CaF_2; $\alpha = x, y,$ or z.

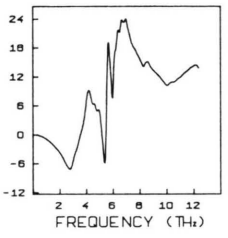
This curve may be used when looking for resonance modes in connection with substitutional imperfections which with some confidence may be depicted as a mass defect; e.g. when tentatively diagnosing low-lying vibronics in the fluorescence spectra of divalent rare earth ions imbedded in a CaF_2 matrix.

** Upon comparison the difference between frequency values obtained by direct diagonalization and by first order perturbation theory proved to be negligible with respect to the level of numerical accuracy maintained (single precision), which finding may serve as an additional certification of the method of GILAT.

22 O. RA, Phys. Stat. Sol. **39**, 265 [1970].



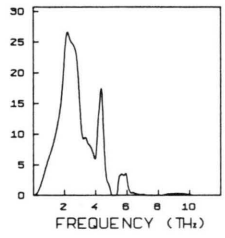
2 a



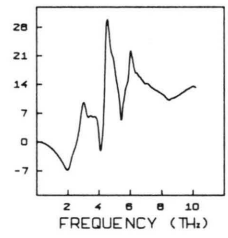
2 b

Fig. 2a. — $\omega^2 M_{01}$ Im $G_0(l1\alpha, l1\alpha; \omega_L^2 x + iO)$ for Sr^{2+} in SrF_2.

Fig. 2b. $\omega^2 M_{01}$ Re $G_0(l1\alpha, l1\alpha; \omega_L^2 x + iO) \cdot 10$ for Sr^{2+} in SrF_2.



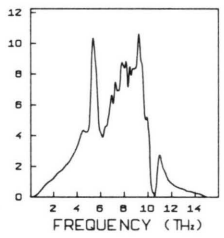
3 a



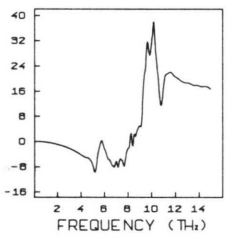
3 b

Fig. 3a. — $\omega_L^2 M_{01}$ Im $G_0(l1\alpha, l1\alpha; \omega_L^2 x + iO)$ for Ba^{2+} in BaF_2.

Fig. 3b. $\omega^2 M_{01}$ Re $G_0(l1\alpha, l1\alpha; \omega_L^2 x + iO) \cdot 10$ for Ba^{2+} in BaF_2.



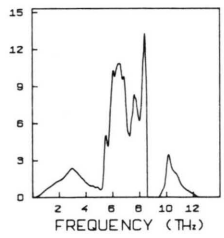
4 a



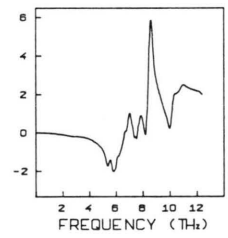
4 b

Fig. 4a. — $\omega_L^2 M_{02}$ Im $G_0(l2\alpha, l2\alpha; \omega_L^2 x + iO)$ for F^- in CaF_2.

Fig. 4b. $\omega^2 M_{02}$ Re $G_0(l2\alpha, l2\alpha; \omega_L^2 x + iO) \cdot 10$ for F^- in CaF_2.



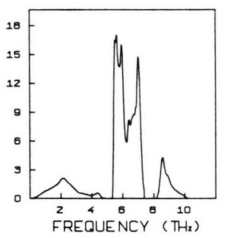
5 a



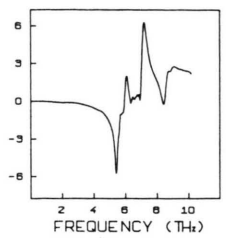
5 b

Fig. 5a. — $\omega_L^2 M_{02}$ Im $G_0(l2\alpha, l2\alpha; \omega_L^2 x + iO)$ for F^- in SrF_2.

Fig. 5b. $\omega^2 M_{02}$ Re $G_0(l2\alpha, l2\alpha; \omega_L^2 x + iO)$ for F^- in SrF_2.



6 a



6 b

Fig. 6a. — $\omega_L^2 M_{02}$ Im $G_0(l2\alpha, l2\alpha; \omega_L^2 x + iO)$ for F^- in BaF_2.

Fig. 6b. $\omega^2 M_{02}$ Re $G_0(l2\alpha, l2\alpha; \omega_L^2 x + iO)$ for F^- in BaF_2.

gradually reduced until all the a_n values had "settled down". The choice $N_a = 149$ was made by the computer while acting on an instruction to continue the computation of a_n's, for all six

$$\text{Im}\, G_0(l\varkappa\alpha, l\varkappa\alpha; \omega_L^2 x + iO)\text{'s},$$

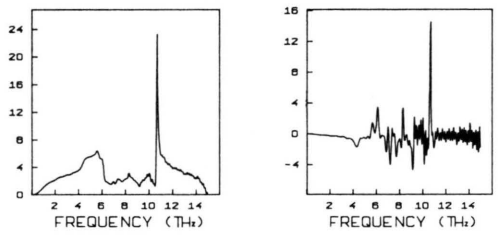
until the right hand side of Eq. (14) differed from unity by less than $0.1\,\%$ in all six cases simultaneously. Each of the resulting truncated sine series expansions accounts for $\sim 99.9\,\%$ of the length in $\mathscr{L}^2(0,1)$ attributed to the corresponding numerically given function by Newton-Cotes quadrature. Figs. 1—6 resolve quite well the prominent peaks and slope discontinuities of the parent numerical representations. However, at $N_a = 149$ a pointwise convergence to the extent required in obtaining a reliable estimate of

$$(\mathrm{d}/\mathrm{d}x)\, \text{Im}\, G_0(l\varkappa\alpha, l\varkappa\alpha; \omega_L^2 x + iO)$$

is not always secured. Consider the CaF_2

$$\text{Im}\, G_0(l1\alpha, l1\alpha; \omega_L^2 x + iO),$$

with α set equal to either of x, y, z and with $\varkappa = 1$ denoting a cation site, in the vicinity of the upper band edge, Fig. 1a. The parent representation exhibited a rather smooth behaviour in this region. Smoothness is not recovered for $N_a = 149$. Instead, kinks appear, a deficiency which is inherited by $\text{Re}\, G_0(l1\alpha, l1\alpha; \omega_L^2 x + iO)$; Fig. 1b. It follows from Eq. (11) that this may seriously reduce the uselfulness of the sine series expansion in calculations on the $\Delta F(\omega^2)$ [$= F(\omega^2) - F_0(\omega^2) =$ change in the density of states] brought about by a defect involving Ca^{2+} sites. A Be^{2+} ion residing at a host lattice cation site is a case in point. When treated as a mass defect this imperfection gives rise to a $\Delta F(\omega^2)$ the $N_a = 149$ version of which is shown in Fig. 7b. Apart from the main pseudolocalized mode



7 a 7 b

Fig. 7a. $-\omega_L^2 M_{01}\,\mathrm{Im}\,G(l1\alpha, l1\alpha;\ \omega_L^2 x + iO)$ for Be^{2+} in CaF_2.

Fig. 7b. $3\,n\,N\,\Delta F(\omega^2)\cdot 10^{-1}\,\omega_L^2$ for Be^{2+} in CaF_2.

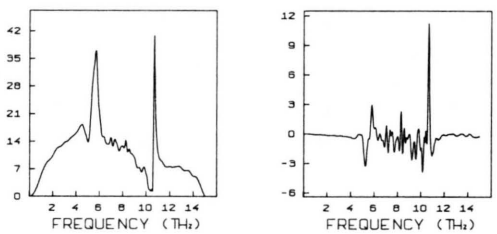
peak at ~ 10.7 THz, the entire structure above 10.0 THz is spurious. There being no differentiation process involved in the construction of defective lattice GF's from perfect lattice GF's when $\omega^2 \in B$, $\mathrm{Im}\,G(l1\alpha, l1\alpha;\ \omega_L^2 x + iO)$ is to a far lesser extent marred by spurious structure, Fig. 7a. As compared to false effects showing up in real parts of in band perfect lattice GF's, incomplete pointwise convergence of Eq. (6) is of relatively little consequence to perfect lattice out of band functions; which fortunate circumstance connects with the removal of the Cauchy principal part restriction. In point of fact, at $N_a = 149$ the approximations to CaF_2, SrF_2, and BaF_2 GF's for $\omega^2 \notin B$ are sufficiently good to lead to satisfactory estimates of first derivatives. To substantiate this contention we make use of the fact that a mass defect treatment of an isolated substitutional Be^{2+} ion in CaF_2 predicts the occurrence of a triply degenerate Γ_{15} type localized mode at 17.55 THz. This local mode, the calculated frequency value of which was confirmed by use of the aforementioned Houston-type and direct summation methods, adds a δ-function(al) to the continuum part of $\mathrm{Im}\,G(l1\alpha, l1\alpha;\ \omega_L^2 x + iO)$. By the imperfect lattice counterpart of Eq. (1), by the well known equation $\boldsymbol{G} = \boldsymbol{G}_0 + \boldsymbol{G}_0 \delta \boldsymbol{L} \boldsymbol{G}$, and by the theory of residues at simple poles of quotients of analytic functions, the strength of the δ-function and thereby the sum

$$SU = \sum_{r=1} U(l1\alpha; r)\, U(l1\alpha; r),$$

where $U(l1\alpha; r)$ is a defect site component of the mass weighted amplitude vector of the rth defective lattice normal mode, depends on

$$(\mathrm{d}/\mathrm{d}x)\, G_0(l1\alpha, l1\alpha;\ \omega_L^2 x)$$

taken at $x_{\text{local mode}}$. At $N_a = 149$ Eqs. (6, 7a, 9b) lead to $SU = 1.005$, which number receives a contribution of 0.769 from the local mode alone. Having subjected the evaluation of the continuum part of SU to a separate control based on the application of numerically given perfect lattice GF's, we rule out the possibility of the good agreement with the ideal result $SU = 1$ being fortuitous and due to a cancelling out of two errors. To test the effect of truncating the sine series expansion of transoptical $(\mathrm{d}/\mathrm{d}x)\, G_0(l1\alpha, l1\alpha;\ \omega_L^2 x)$'s at some distance from ω_L we turn to a U-center in CaF_2. It is by now generally acknowledged that an inclusion of force field alterations is essential to an adequate description of this kind of imperfection. However, this does not in the present context detain us from depicting the substitutional H^- "ion" as a mass defect. As



8 a 8 b

Fig. 8a. $-\omega_L^2 M_{02}\,\mathrm{Im}\,G(l2\alpha, l2\alpha;\ \omega_L^2 x + iO)\cdot 10$ for H^- in CaF_2.

Fig. 8b. $3\,n\,N\,\Delta F(\omega^2)\cdot 10^{-1}\,\omega_L^2$ for H^- in CaF_2.

expected the predicted local mode frequency 36.61 THz is at variance with the experimental 20 °K value 28.95 THz,[23]. This time the calculated SU equals 0.999, the local mode part amounting to 0.996. The introduction of substitutional ions into the BaF_2 (model) lattice provides us with an opportunity to study the properties of

$$(\mathrm{d}/\mathrm{d}x)\, G_0(l1\alpha, l1\alpha;\ \omega_L^2 x) \quad \text{for} \quad \omega^2 \in [\tilde{B} \cap (0, \omega_L)].$$

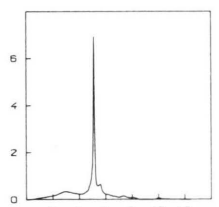
As revealed by Figs. 3a, 6a the latter set is in the BaF_2 case non-empty and consists of two gaps in the frequency spectrum. As a probe we apply a substitutional Mg^{2+} ion (in the mass defect approximation) to find three localized modes; the first in the lower gap at 5.25 THz, the second in the upper gap at 7.82 THz, and the third in the transoptical region at 10.60 THz. The corresponding SU contributions are 0.041, 0.314, and 0.421, respectively. The total calculated SU equals 1.000. Thus, despite occurrences

[23] R. J. Elliot, W. Hayes, G. D. Jones, H. F. MacDonald, and C. T. Sennet, Proc. Roy. Soc. London **A 289**, 1 [1965].

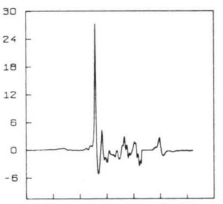
of inaccurate pointwise behaviour of

$$\text{Im } G_0(l\varkappa\alpha, l\varkappa\alpha; \omega_L^2 x + iO)$$

and of Re $G_0(l\varkappa\alpha, l\varkappa\alpha; \omega_L^2 x + iO)$ a truncation at $N_a = 149$ does not seem to preclude a reasonable representation of $G_0(l\varkappa\alpha, l\varkappa\alpha; \omega_L^2 x)$ and even of $(d/dx)\, G_0(l\varkappa\alpha, l\varkappa\alpha; \omega_L^2 x)$ for the crystals in question. Therefore, since the preceding statement was found to apply equally well to off-diagonal core-core, core-shell, and to shell-shell GF's, the calculation of local mode frequencies and of local mode contributions to defective lattice GF's, and thereby to correlation functions, seems to be well in hand (except, perhaps, for a local mode emerging in the extreme vicinity of a band edge). Also, when appearing as parts of integrands the approximations to both perfect and imperfect lattice in-band GF's would seem to be quite trustworthy. As for perfect lattice GF's of purely imaginary arguments these too, when approximated by a finite series, see Eq. (9c), are relatively insensitive to the detailed behaviour of Im $G_0(l\varkappa\alpha, l'\varkappa'\beta; \omega_L^2 x + iO)$. For large y this is evident from Eq. (1). For small, but not necessarily for extremely small[24], y it follows, in the present cases, from the absence of spurious structure in Im $G_0(l\varkappa\alpha, l'\varkappa'\beta; \omega_L^2 x + iO)$'s toward the low-frequency end. This is fortunate, since in calculating thermodynamic state functions we may now take refuge in (the general version of) Eq. (10) or in expressions for thermodynamic quantities derived by MONTROLL and POTTS[25] who used contour integration techniques. Thus, we are relieved of the task of attempting to rectify erroneous $\Delta F(\omega^2)$'s of the type shown in Fig. 7b. An attempt to improve a $\Delta F(\omega^2)$ by direct numerical smoothing would in many cases be hazardous, since it might be difficult to distinguish false structures from genuine ones. For instance, on the face of it the peaks between ~ 9 THz and ~ 10 THz in Fig. 7b are very similar to the ones above the main maximum at ~ 10.7 THz. Nevertheless, the former are genuine and should not be removed, whereas the latter represent mere "numerical noise". It should be borne in mind at this point that while absolute thermodynamic state functions are insensitive to occurrences of false details as well as to lacks of real details in calculated frequency spectra, this is not the case for defect induced changes in thermodynamic quantities as calculated from $\Delta F(\omega^2)$'s. A successful outcome of an integration involving a $\Delta F(\omega^2)$ hinges on a "detailed balancing" of contributions of different signs. At the very least, a smoothed in-band $\Delta F(\omega^2)$ ought, in the case of an imperfection leaving unchanged the total number of degrees of freedom, to comply with the requirement that the integrated $\Delta F(\omega^2)$ be practically zero. As for attempts to rid $\Delta F(\omega^2)$ of spurious peaks by smoothing of underlying in-band GF's, one should be careful not to violate severely the closure conditions expressed by Eq. (14). At all events, neither smoothing of $\Delta F(\omega^2)$'s or GF's nor attempts[26] to improve $\Delta F(\omega^2)$'s by increasing N_a values beyond those dictated by a suitable "numerical interpretation" of Eq. (14) seem warranted by a need for numerical data on the vibrational contributions to the thermodynamics of imperfect crystals. This assertion finds support in the following examples. Within the mass defect approximation the introduction of an isolated substitutional Cl^- ion into SrF_2 is accompanied by a $\Delta F(\omega^2)$, the $N_a = 149$ version of which is shown in Fig. 9b. A visual inspection of this figure leads



9a



9b

Fig. 9a. $-\omega_L^2 M_{02}$ Im $G(l2\alpha, l2\alpha; \omega_L^2 x + iO) \cdot 10^{-1}$ for Cl^- in SrF_2.

Fig. 9b. $3\,n\,N\,\Delta F(\omega^2) \cdot 10^{-1}\,\omega_L^2$ for Cl^- in SrF_2.

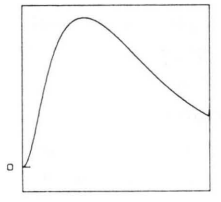
to the impression that whatever lack of pointwise convergence there might be, it is comparatively harmless in this case. This conjecture is corroborated by the fact that integrations involving $\Delta F(\omega^2)$ did eventually produce results for the change in Helmholz free energy which very nearly coincided with values obtained from Eqs. (10), (12) at the temperatures investigated; -374 and -605 cal mole^{-1}

[24] See next section.

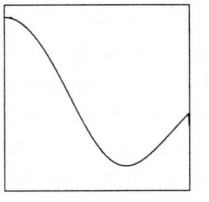
[25] E. W. MONTROLL and R. B. POTTS, Phys. Rev. **100**, 525 [1955].

[26] The phrase "attempts" is in order here, since it has not as yet been proved that (d/dx) Im $G_0(l\varkappa\alpha, l'\varkappa'\beta; \omega_L^2 x + iO)$ and (d/dx) Re $G_0(l\varkappa\alpha, l'\varkappa'\beta; \omega_L^2 x + iO)$ can be evaluated by term by term differentations.

at 150 and 298 °K, respectively. Also, a $\Delta F(\omega^2)$ based change in zero point energy was in agreement with the value found by use of the Montroll-Potts relation[25]; -283 cal mole^{-1}. However, in terms of computational speed self seeking polynomial $\Delta F(\omega^2)$ integrations proved inferior by a factor exceeding 10^{27} in all three cases. In view of the large ω_n behaviour of the summands of Eq. (10)[7], and the difference in behaviour between the curves in Fig. 10a and Fig. 9b, this is hardly surprising.



10 a



10 b

Fig. 10a. A substitutional Be^{2+} ion in CaF_2. The integrand appearing in the Montroll-Potts equation for the change in zero point energy after mapping of the integration range $(0, \infty)$ on to $(0, 1)$ by the transformation $\sqrt{y} = t/(t-1$, Arbitrary scale.

Fig. 10b. A substitutional Cl^- ion in SrF_2. The integrand appearing in the Montroll-Potts equation for the change in zero point energy after mapping of the integration range $(0, \infty)$ on to $(0, 1)$ by the transformation $\sqrt{y} = t/(t-1$, Arbitrary scale.

Moreover the convenience of schemes which avoid using $\Delta F(\omega^2)$ is hardly a feature depending critically on the approximate SrF_2

$$\mathrm{Im}\, G_0(l\varkappa\alpha, l\varkappa\alpha; \omega_L^2 x + iO)\text{'s}$$

being pointwise well-behaved, as compared to their CaF_2 counterparts say. Reverting to the system $CaF_2:Be^{2+}$ it will be recalled that the false structure in $\Delta F(\omega^2)$, Fig. 7b, stems from the equally false but less accentuated kinks in the CaF_2

$$\mathrm{Im}\, G_0\,(l1\alpha, l1\alpha; \omega_L^2 x + iO)\,,$$

which function determines also $G_0(l1\alpha, l1\alpha; -\omega_L^2 y)$. However, in keeping with a previous remark a comparison of Fig. 10a with Fig. 10b reveals that the aforementioned Montroll-Potts formula is equally amenable to numerical analysis in either case $CaF_2:Be^{2+}$ or $SrF_2:Cl^-$. The same conclusion applies to Eq. (10) and to the various contour integration formulas.

The author does not question the value of Dyson's formula Eq. (11) as a theoretical tool. To do so would indeed be foolhardy in view of its playing a crucial role in lattice dynamics of imperfect crystals. In addition, it may be useful even on the practical level if a plot of $\Delta F(\omega^2)$ is sought for the purpose of diagnosing resonance modes, say. On the other hand, painstaking efforts to refine calculated $\Delta F(\omega^2)$'s in connection with work on numerical values for thermodynamic state functions would, in most cases, seem unjustified, since such functions are usually better dealt with by other methods.

Before closing this section we digress from the computational aspects to dwell briefly on the physics of the above mentioned point defects. In analyzing their data on U-centers in alkaline earth fluorides ELLIOT et al.[23] considered the light anion impurity as vibrating in a tetrahedral rigid anharmonic well. With the potential well parameters fitted to some of the experimentally obtained quantities the model, no doubt, describes satisfactorily local mode properties such as temperature dependent intensity, shift, and width of vibrational lines. Their discussion of sidebands (two-phonon bands stemming from anharmonicity and/or second order electric dipole moment induced coupling of the localized modes with lattice modes; a coupling which causes either an emission or an absorption of a lattice phonon) was based on the assumption of an essentially unperturbed continuum part of the phonon spectrum. In view of the interesting fact that the anion site symmetry ($T_d = \bar{4}3$ m) imposes no symmetry restrictions on the participating phonons[28], which lack of selection rules implies an intimate correspondence between the sidebands and the frequency distribution, it seems pertinent to reconsider the assumption of an undeformed spectrum. Some perturbation of a majority of continuum phonons which in the perfect lattice case receive contributions from F^- motion is inevitable, if only because of the closure conditions on the mass weighted

[27] It is quite likely that this number could be somewhat reduced by choosing other integration procedures. However, in the author's opinion one would not gain any advantage by efforts in this direction. Admittedly, the efficiency of the recipe given by Eq. (10) deteriorates markedly with very low temperatures coming into play. However, since there is a special low-temperature free energy expansion based on contour integration available[11], the inadequacy of Eq. (10) in the low-temperature region provides no reason for reverting to $\Delta F(\omega^2)$.

[29] Actually the $BaF_2:H^-(D^-)$ mode referred to is nominally a localized gap mode rather than a pseudolocalized mode. However, its frequency is quite close to the upper edge of the upper gap[22] and physically there would be little distinction from pseudolocalization because of anharmonicity.

normal mode vectors in conjunction with the large $H^-(D^-)$ amplitude in the localized mode. The crucial point is whether the impurity effects are sufficiently strong to precipitate resonance modes or gap modes which might be expected to show up in the sideband structure. ELLIOT et al. state[23] that the form of light mass defects in question is unlikely to introduce low-frequency resonances. This is borne out by Fig. 8a, b. On the other hand, in so far as the mass defect approximation can be trusted in a qualitative sense, a high-frequency semilocalized mode appears in all three systems: $CaF_2:H^-(D^-)$, $SrF_2:H^-(D^-)$, $BaF_2:H^-(D^-)$. This follows from Fig. 8a, b and similar calculations on $SrF_2:H^-(D^-)$ and $BaF_2:H^-(D^-)$[29]. However, as can be inferred from Fig. 4, Fig. 8, and similar curves for the two other systems, the semilocalized modes occur at frequency values close to the main peak in the longitudinal optical part of the perfect lattice density of one-phonon states. They would, if they exist, be hard to detect as distinct physical occurrences, and their main effect on sidebands would be to increase the heigth and width of the longitudinal optical peak. Presumably, the existence of such an augmentation effect would have to be verified theoretically. The inference from theoretical work on U-center sidebands in alkali halides[30, 31] is that quantitative calculations of peak shapes still seem to be a little beyond the present status of the art. Conceivably, the emerging of semilocalized modes of frequency values between those of the transverse and longitudinal optical long wave modes might also be impeded by the existence of lossy polariton modes in this region.

With regard to the systems $CaF_2:Be^{2+}$, $SrF_2:Cl^-$, and $BaF_2:Mg^{2+}$, these would seem to be worth while subjects of experimental spectroscopic studies. In particular, IR work on SrF_2 doped with $SrCl_2$ might prove to be an interesting extension of the measurements on mixed CaF_2-SrF_2 and SrF_2-BaF_2 crystals carried out by VERLEUR and BARKER[32].

5. Concluding Remarks

The extrapolation approach to frequency distributions being already in existence at the time, the sine series procedure for frequency spectra was presented by AGGARWAL et al.[16] as a competitive method. Both schemes carrying over to the evaluation of GF's, the scorecards now run somewhat as follows:

i) The extrapolation method can be efficiently implemented while invoking only simple and, more important, safe numerical techniques. To the extent that its applicability to moderately complex lattices can be assessed from the alkaline earth halide results, it leads to a good resolution of minute details in spectra and GF's without excessive computational effort. AGGARWAL et al. argue that the extrapolation method requires prior knowledge about the location in $\boldsymbol{k}$-space of critical points. However, this does not seem to entail a major deficiency. The symmetry set of critical points, which in many cases constitutes a substantial portion of the total set of such points, can be determined without much effort by what is now a standard juxtaposition of symmetry and connectivity arguments[33]. Moreover a critical point analysis comprising a search for the minimal set would frequently have a natural place in a lattice dynamics investigation. In the author's opinion the basic disadvantage of using exclusively the extrapolation method originates from the simple fact that a quasicontinuous numerical representation requires a very extensive tabulation of discrete GF values. A fairly realistic description of even a simple isolated (non-isotopic) point defect usually calls for an appreciable number of GF's, particularly if deformable atoms or ions be involved. The attendant problems of accommodating, transmitting, and using many numerically given GF's concurrently pose a difficulty even with access to a modern digital computer.

ii) Inasmuch as $\mathrm{Im}\, G_0(l\varkappa\alpha, l'\varkappa'\beta;\ \omega_L^2 x + iO)$ enters the defect theory primarily in a distributional context it seems logical to judge a trigonometric polynomial approximation to this function first of all by its properties as (the generator of) a functional. Upon choosing as a criterion an accurate reproduction of values at functions which are constants on (0, 1) [see Eq. (14)], and upon computing Fourier coefficients enough to meet this requirement, CaF_2, SrF_2, and BaF_2 N_a's remain sufficiently small to lead to a significant compaction of the amount of data that must be stored. As follows from the preceding section the resulting finite sets of Fourier

[28] R. LOUDON, Proc. Phys. Soc. London **84**, 379 [1964].
[30] N. X. XINH, Phys. Rev. **163**, 896 [1967].
[31] J. B. PAGE and B. G. DICK, Phys. Rev. **163**, 910 [1967].
[32] H. W. VERLEUR and A. S. BARKER, Phys. Rev. **164**, 1169, [1967].
[33] J. C. PHILLIPS, Phys. Rev. **104**, 1263 [1956].

coefficients contain sufficient information to enable one to deal with a variety of defect properties. In addition, one may list as a bonus the replacement of a numerical table by a simple analytic form. This replacement simplifies the calculation of principle value integrals [see Eqs. (2), (3), (7a)]. Also, in the case of an isolated mass defect in a diagonally cubic lattice we have seen that alterations in even moments of the frequency distribution may be obtained directly from the Fourier coefficients by means of a recurrence relation, which finding has bearing on the evaluation of defect induced changes in thermodynamic state functions. Among the shortcomings of the sine series approach there are two of minor importance. First, and as previously mentioned estimates of $(\mathrm{d}/\mathrm{d}x)\,\mathrm{Im}\,G_0(l\varkappa\alpha, l'\varkappa'\beta; \omega_\mathrm{L}^2 x + iO)$ and $(\mathrm{d}/\mathrm{d}x)\,\mathrm{Re}\,G_0(l\varkappa\alpha, l'\varkappa'\beta; \omega_\mathrm{L}^2 x + iO)$ obtained by term by term differentiation of finite right hand sides of Eqs. (6), (7a) ($x < 1$) can be unreliable. The attendant effect on $\Delta F(\omega^2)$, at least, does not add seriously to the computational problems of defect work since $\Delta F(\omega^2)$ is in itself usually not very well suited to numerical treatment. The second disadvantage connects with any finite version of the right hand side of Eq. (6) behaving like x^1 as $x \to 0$. Consider for a moment the cubic Bravais lattices. The diagonal $\mathrm{Im}\,G_0(l\varkappa\alpha, l\varkappa\alpha; \omega_\mathrm{L}^2 x + iO)$'s of these lattices are known to coincide with the frequency distribution to within a constant factor[2]. However, a truncated sine series expansion, the argument of which is $x(=(\omega/\omega_\mathrm{L})^2)$ cannot approach a Debye spectrum asymptotically when $x \to 0$. Changing to ω as the primary argument one finds $\mathrm{Im}\,G_0(l\varkappa\alpha, l\varkappa\alpha; \omega + iO) \sim \omega^3$ and not the correct $\sim \omega^2$ behaviour in the limit $\omega \to 0$. Accordingly, Eq. (6) may lead to inaccurate results for quantities which are susceptible to changes in the small-x behaviour of

$$\mathrm{Im}\,G_0(l\varkappa\alpha, l\varkappa\alpha; \omega_\mathrm{L}^2 x + iO);$$

e.g. the low-temperature properties of thermal contributions to correlation functions. However, by letting the sine function expression dovetail to a power series taking over at some small frequency value, or by suitably redefining x [$x = (\omega/\omega_\mathrm{L})^{3/2}$, say], this problem is readily eliminated. It is the author's experience that serious difficulties are encountered in working out sine series representations of imaginary parts of in-band GF's only if Fourier coefficient computation is made dependent on BZ integrations.

It follows from the above considerations that both the sine series expansion and the adapted extrapolation procedure are useful schemes for the evaluation of lattice Green's functions when regarded as complementary methods.

Acknowledgement. The author is indebted to Norges Teknisk-Naturvitenskapelige Forskningsrad for financial support.