PHYSICAL REVIEW B VOLUME 26, NUMBER 8 15 OCTOBER 1982

Dipole-field sums and Lorentz factors for orthorhombic lattices, and implications for polarizable molecules

C. K. Purvis
National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio 44135

P. L. Taylor
Case Western Reserve University, Department of Physics, Cleveland, Ohio 44106
(Received 24 May 1982)

The relationship between dipole-field sums and Lorentz tensor components in single crystals is described and used to develop a method for computing the tensor components via rapidly convergent sums of Bessel functions. The method is used to compute Lorentz factors for simple, body-centered, and base-centered orthorhombic lattices and derivatives Lorentz factors for simple orthorhombic lattices. Both the Lorentz factors and their derivatives are found to be very sensitive to lattice structure. The Lorentz-factor formalism is used to derive the equivalent of the Clausius-Mossotti relation for general orthorhombic lattices and to relate permanent molecular dipole moment to crystal polarization for the case of a ferroelectric of polarizable point dipoles. It is found that the polarization "enhancement" due to self-polarization familiar from classical theory may actually be a reduction (i.e., $P<P_0$) in consequence of negative Lorentz factors in one or two lattice directions for noncubic crystals.

I. INTRODUCTION

This paper considers the dependence of the internal electric field in a single crystal on crystal structure and changes in the field under small deformations. The crystal is assumed to be orthorhombic and either homogeneously polarized or resolvable into two or more homogeneously polarized sublattices. Of particular interest is the field at a lattice site, which is the internal field acting to polarize a molecule in the crystal.

The formalism chosen is that of depolarization and Lorentz tensors, which has been described by Colpa.[1] Herein, advantage is taken of the fact that the depolarization tensor is known for certain macroscopic shapes and since the Lorentz tensor depends only on crystal structure and observation point within the unit cell, its components can be expressed as dipole sums. These dipole sums are then transformed into rapidly convergent sums of Bessel functions. The method has the advantage of providing explicit expressions for the Lorentz tensor components which display the tensor's symmetries clearly.

II. DIPOLE SUMS AND LORENTZ FACTORS

A. Formalism and method

The electric field $\vec{E}_{\rm dip}(\vec{r})$ at a point $(\vec{r})$ inside a crystal, each of whose lattice sites is occupied by an electric point dipole of moment $\vec{p}$, is just the sum of the fields at $\vec{r}$ due to each dipole in the sample. The field $\vec{E}_{\rm dip}(\vec{r})$ is linearly related to the polarization $\vec{P}$ of the crystal, $\vec{P}=n\vec{p}$ with n the number of dipoles per unit volume, through the symmetric dipole sum tensor[1] $\tilde{C}$:

$$\vec{E}_{\rm dip}(\vec{r})=\frac{\alpha_0}{\epsilon_0}\tilde{C}(\vec{r})\vec{P}\ , \tag{1}$$

where $\alpha_0=4\pi$ for Gaussian units and $\alpha_0=1$ for rationalized meter-kilogram-second (mks) units, $\epsilon_0=1$ for Gaussian units, and $\epsilon_0=8.85\times10^{-12}$ farad m^{-1} in rationalized mks units. The components of $\tilde{C}$ are given by

$$C_{kl}=(4\pi n)^{-1}{\sum_{\vec{r}'}}''\partial'_{kl}\left[\frac{1}{|\vec{r}-\vec{r}'|}\right], \tag{2}$$

where ∂'_{kl} is a second derivative operator on $\vec{r}'$ with respect to Cartesian components k and l, and the

double prime on the summation indicates that the sum extends over all positions $\vec{r}'$ of dipoles inside the crystal, omitting terms for which $\vec{r}'=\vec{r}$.

Evidently, $\tilde{C}$ depends on both the microscopic parameters, i.e., the crystal structure, and the macroscopic ones, i.e., the shape. The essence of the formalism of depolarization and Lorentz tensors is the decomposition of $\tilde{C}$ into a linear sum of two tensors, denoted $\tilde{D}$ and $\tilde{L}$. The depolarization tensor $\tilde{D}$ depends only on the macroscopic parameters and the location of $\vec{r}$ in the crystal, while the Lorentz tensor $\tilde{L}$ depends only on the microscopic parameters and the position of $\vec{r}$ in the unit cell. In terms of the depolarization and Lorentz tensor components, the components of the dipole sum tensor are expressed as[1]

$$C_{kl}(\vec{r})=L_{kl}(\vec{r})-D_{kl}(\vec{r}) . \tag{3}$$

The choice of $\tilde{D}$ to represent the depolarization tensor follows the notation of Colpa.[1] However, it is sometimes denoted by $\tilde{N}$ or $\tilde{N}/4\pi$ in the literature. The principal values of $\tilde{D}$ are known as the depolarization factors, and those of $\tilde{L}$ as the Lorentz factors. The following sum rules apply:

$$\begin{aligned} &C_{xx}(\vec{r})+C_{yy}(\vec{r})+C_{zz}(\vec{r})=0 , \\ &D_{xx}(\vec{r})+D_{yy}(\vec{r})+D_{zz}(\vec{r})=1 , \\ &L_{xx}(\vec{r})+L_{yy}(\vec{r})+L_{zz}(\vec{r})=1 , \end{aligned} \tag{4}$$

from Ref. 1, Refs. 1–3, and Refs. 1 and 8, respectively.

It is well known that if the crystal is taken to be ellipsoidal, with its principal axes along $\hat{x}$, $\hat{y}$, and $\hat{z}$, the depolarization tensor is diagonal and independent of position. This is equivalent to the statement that a uniformly polarized ellipsoid produces a uniform depolarizing field. Depolarization factors for ellipsoids have been tabulated by Stoner[2] and by Osborn.[3] In the calculation of Lorentz tensor components, the fact that one or two of the depolarization factors are zero for the limiting "needle" and "coin" shaped ellipsoids of revolution is used.

The Lorentz tensor components are independent of the overall crystal shape and the direction of polarization[1]; they depend only on the relative lattice spacings and the location of $\vec{r}$ in the unit cell. Thus it is possible to consider a different crystal shape, orientation, and polarization direction for each combination of (k,l) in Eq. (3). With appropriate choices of these macroscopic parameters, D_{kl} can be made equal to zero for any given (k,l). Then the Lorentz tensor component can be calculated directly from the appropriate dipole sum. Because appropriate shapes for setting $D_{kk}=0$ involve letting one or two of the crystal dimensions become macroscopically small (although they must remain microscopically large), it is necessary to transform the slowly convergent dipole sums into ones which converge rapidly.

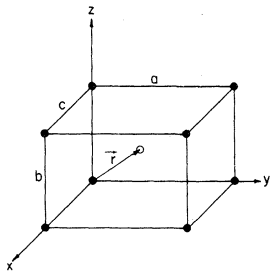

FIG. 1. Orthorhombic unit-cell coordinates and lattice spacings, with field observation point indicated.

The method is most easily illustrated by example. The coordinate system chosen is illustrated in Fig. 1. The origin is at a lattice site of a simple orthorhombic lattice with lattice spacings c,a,b in $\hat{x},\hat{y},\hat{z}$, respectively. The observation point is $\vec{r}=(x,y,z)$. To calculate the Lorentz factor L_{xx} $(\equiv L_{cc})$, one imagines a needle-shaped crystal with its long axis and polarization both in the $\hat{x}$ direction. The point dipoles are located at $\vec{r}'=(jc\hat{x}+ka\hat{y}+lb\hat{z})$. Because of the needle shape, the index j ranges from minus to plus infinity while k and l have finite range, but are at least several tens. The lattice has been stipulated to be simple, so there is only one dipole per unit cell and $n=(abc)^{-1}$. The depolarization factor D_{xx} equals zero for this needle-shaped crystal, so

$$L_{cc}(\vec{r})=\frac{abc}{4\pi}\sum_{k,l}\sum_{j=-\infty}^{\infty}\left\{\frac{3(x-jc)^2}{[(x-jc)^2+(y-ka)^2+(z-lb)^2]^{5/2}}-[(x-jc)^2+(y-ka)^2+(z-lb)^2]^{-3/2}\right\} . \tag{5}$$

Analogous expressions for the other two Lorentz factors are obtained by imagining needle-shaped crystals with long axes and polarization along $\hat{y}$ and $\hat{z}$.

Because the off-diagonal elements of $\tilde{D}$ are zero for any ellipsoid, the choice of shape for calculation of off-diagonal Lorentz tensor components is not critical. The symmetry of $\tilde{L}$ is most clearly seen by choosing a disc shape or "coin." For example, to compute L_{xy} ($\equiv L_{ca}$), a disc lying in the x-y plane may be imagined. Then

$$L_{ca}(\vec{r})=\frac{abc}{4\pi}\sum_{l}\sum_{j,k=-\infty}^{\infty}\frac{3(x-jc)(y-ka)}{[(x-jc)^2+(y-ka)^2+(z-lb)^2]^{5/2}} . \tag{6}$$

Here the sum on l is finite so that a rapidly converging equivalent to the j and k sum is needed. The symmetry of the Lorentz tensor is evident from Eq. (6); clearly $L_{ca}=L_{ac}$. Expressions for L_{cb} and L_{ab} are derived similarly.

Transformation of the dipole sums in Eqs. (5) and (6) into rapidly convergent sums is carried out in the next section. Before proceeding, however, it is useful to make a few observations. First, although the Lorentz tensor components have been evaluated by imagining particular crystal shapes, they are particular only to the lattice structure and observation point within the unit cell, and are thus quite generally applicable. Second, Lorentz tensor components for more complex lattice structures can be found by superposition. For example, at a lattice site of a body-centered (bc) orthorhombic lattice,

$$L_{kl}^{(\mathrm{bc})}=\tfrac{1}{2}[L_{kl}^{(s)}(0,0,0)+L_{kl}^{(s)}(c/2,a/2,b/2)] ,$$

where the (s) superscript indicates the simple orthorhombic lattice, and lattice spacings c,a,b in $\hat{x},\hat{y},\hat{z}$, respectively, have been assumed. The factor of $\frac{1}{2}$ arises because there are now two dipoles per unit cell. It will turn out for this case that the Lorentz tensor is diagonal.

B. Transformation of sums

To obtain useful expressions for the Lorentz tensor components, rapidly convergent equivalents to the dipole sums in Eqs. (5) and (6) are needed. The method chosen is similar to those of Van der Hoff and Benson[4] and of Tripathy *et al.*[5] and proceeds by evaluation of three generalized sums for $n>0$. These are

$$\mathscr{S}_{(\rho,s,d)}^{(n)}\equiv\sum_{m}[\rho^2+(s-md)^2]^{-n/2} , \tag{7a}$$

$$S_{(\rho,s,d)}^{(n)}\equiv\sum_{m}\frac{(s-md)^2}{[\rho^2+(s-md)^2]^{-n/2}} , \tag{7b}$$

$$\Sigma_{(\rho,s,s',d,d')}^{(n)}\equiv\sum_{m,m'}\frac{(s-md)(s'-m'd')}{[\rho^2+(s-md)^2+(s'-m'd')^2]^{-n/2}} , \tag{7c}$$

where $0\le s\le d$, $0\le s'\le d'$, and the indices m and m' take on all integer values $(0,\pm1,\pm2,\ldots)$.

Evaluation of each sum proceeds by use of a representation of the gamma function,[6]

$$\Gamma(z)=\mu^z\int_0^\infty t^{z-1}e^{-\mu t}dt \quad (\mathrm{Re}z>0,\ \ \mathrm{Re}\mu>0) , \tag{8}$$

the Poisson summation formula,

$$\sum_{m}f(m)=\sum_{h}\int_{-\infty}^{\infty}e^{2\pi ihx}f(x)dx , \tag{9}$$

and an integral representation[7] of the modified Bessel function of the second kind of order ν,

$$K_\nu(2\sqrt{\beta\gamma})=\frac{1}{2}\left[\frac{\gamma}{\beta}\right]^{\nu/2}\int_0^\infty t^{\nu-1}e^{-(\beta/t)-\gamma t}dt \quad (\mathrm{Re}\beta>0,\ \ \mathrm{Re}\gamma>0) . \tag{10}$$

Let us first consider the general case in which $\rho>0$, and return later to consider the $\rho=0$ case.

1. Evaluation of $\mathscr{S}^{(n)}$

By use of Eq. (8), $\mathscr{S}^{(n)}$ may be cast into the form

$$\mathscr{S}^{(n)}_{(\rho,s,d)}=\frac{1}{\Gamma\left[\frac{n}{2}\right]}\int_0^\infty t^{[(n/2)-1]}e^{-\rho^2 t}\left[\sum_m e^{-(s-md)^2 t}dt\right]. \tag{11}$$

The sum in large parentheses is evaluated by use of Eq. (9):

$$\begin{aligned}\sum_m e^{-(s-md)^2 t}&=\sum_h \int_0^\infty e^{2\pi i h x}e^{-(s-xd)^2 t}dx\\&=\frac{2}{d}\int_0^\infty e^{-y^2 t}dy+\frac{2}{d}\sum_h{}' e^{2\pi i h s/d}\int_0^\infty e^{-y^2 t}\cos\left[\frac{2\pi h y}{d}\right]dy\\&=\frac{\sqrt{\pi}}{d}t^{-1/2}+\frac{\sqrt{\pi}}{d}\sum_h{}' e^{2\pi i h s/d}t^{-1/2}e^{-\pi^2 h^2/d^2 t},\end{aligned}$$

where the prime on the summation sign indicates that the term with $h=0$ is excluded. Substitution back into Eq. (11) yields

$$\begin{aligned}\mathscr{S}^{(n)}_{(\rho,s,d)}=&\frac{\sqrt{\pi}}{d\Gamma\left[\frac{n}{2}\right]}\int_0^\infty t^{(n-3)/2}e^{-\rho^2 t}dt\\&+\frac{\sqrt{\pi}}{d\Gamma\left[\frac{n}{2}\right]}\sum_h{}' e^{2\pi i h s/d}\int_0^\infty t^{(n-3)/2}\exp\left[-\rho^2 t-\frac{\pi^2 h^2}{d^2 t}\right]dt.\end{aligned}$$

The first integral in this expression is just $\Gamma[(n-1)/2])\rho^{-(n-1)}$ for $n>1$, while the second has the form given in Eq. (10). Thus, for $n>1$,

$$\mathscr{S}^{(n)}_{(\rho,s,d)}=\frac{\sqrt{\pi}\Gamma[(n-1)/2]}{d\Gamma\left[\frac{n}{2}\right]\rho^{n-1}}+\frac{2\pi^{n/2}}{d\Gamma\left[\frac{n}{2}\right]}\sum_h{}' e^{2\pi i h s/d}\left[\frac{|h|}{\rho d}\right]^{n/2}K_{(n-1)/2}\left[\frac{2\pi|h|\rho}{d}\right]. \tag{12}$$

2. Evaluation of $S^{(n)}$

Evaluation of $S^{(n)}$ proceeds similarly as follows:

$$S^{(n)}_{(\rho,s,d)}=\frac{1}{\Gamma\left[\frac{n}{2}\right]}\int_0^\infty t^{(n/2)-1}e^{-\rho^2 t}\left[\sum_m (s-md)^2 e^{-(s-md)^2 t}\right]dt.$$

Now

$$\begin{aligned}\sum_m (s-md)^2 e^{-(s-md)^2 t}&=\sum_h \int_{-\infty}^\infty (s-xd)^2 e^{2\pi i h x}e^{-(s-xd)^2 t}dx\\&=\frac{2}{d}\int_0^\infty y^2 e^{-y^2 t}dy+\frac{2}{d}\sum_h{}' e^{2\pi i h s/d}\left[-\frac{\partial}{\partial t}\right]\int_0^\infty e^{-y^2 t}\cos\left[\frac{2\pi h y}{d}\right]dy\\&=\frac{\sqrt{\pi}}{2d}t^{-3/2}+\frac{\sqrt{\pi}}{2d}\sum_h{}' e^{2\pi i h s/d}\left[t^{-3/2}-\frac{2\pi^2 h^2}{d^2}t^{-5/2}\right]\exp\left[-\frac{\pi^2 h^2}{d^2 t}\right],\end{aligned}$$

whence

$$S^{(n)}_{(\rho,s,d)}=\frac{\sqrt{\pi}}{2d\Gamma\left[\frac{n}{2}\right]}\left\{\int_0^\infty t^{(n-5)/2}e^{-\rho^2 t}dt+\sum_h{}' e^{2\pi ihs/d}\left[\int_0^\infty t^{(n-5)/2}\exp\left[-\rho^2 t-\frac{\pi^2h^2}{d^2t}\right]dt\right.\right.$$
$$\left.\left.+\int_0^\infty t^{(n-7)/2}\exp\left[-\rho^2 t-\frac{\pi^2h^2}{d^2t}\right]dt\right]\right\}.$$

The integrals can be done as before to yield, for $n>3$,

$$S^{(n)}_{(\rho,s,d)}=\frac{\sqrt{\pi}\Gamma[(n-3)/2]}{2d\Gamma\left[\frac{n}{2}\right]\rho^{n-3}}+\frac{\pi^{(n/2)-1}}{d\Gamma\left[\frac{n}{2}\right]}\sum_h{}' e^{2\pi ihs/d}\left[\left[\frac{|h|}{\rho d}\right]^{(n-3)/2}K_{(n-3)/2}\left[\frac{2\pi|h|\rho}{d}\right]\right.$$
$$\left.-2\pi\rho^2\left[\frac{|h|}{\rho d}\right]^{(n-1)/2}K_{(n-5)/2}\left[\frac{2\pi|h|\rho}{d}\right]\right]. \tag{13}$$

3. *Evaluation of* $\Sigma^{(n)}(\rho,s,s',d,d')$

$$\Sigma^{(n)}_{(\rho,s,s',d,d')}=\frac{1}{\Gamma\left[\frac{n}{2}\right]}\int_0^\infty t^{(n/2)-1}e^{-\rho^2 t}\left[\sum_{m,m'}(s-md)(s'-m'd')\right.$$
$$\left.\times\exp\left[-(s-md)^2t\right]\exp\left[-(s'-m'd')^2t\right]\right]dt\,. \tag{14}$$

In this form the double sum can be separated into two single sums which can be evaluated separately:

$$\sum_{m,m'}(s-md)e^{-(s-md)^2t}(s'-m'd')e^{-(s'-m'd')^2t}=\sum_m(s-md)e^{-(s-md)^2t}\sum_{m'}(s'-m'd')e^{-(s'-m'd')^2t}\,.$$

Now,

$$\sum_m(s-md)e^{-(s-md)^2t}=\sum_h\int_{-\infty}^{\infty}e^{2\pi ihx}(s-xd)e^{-(s-xd)^2t}dx$$
$$=\frac{1}{d}\sum_h{}' e^{\lambda s}\left[-\frac{\partial}{\partial\lambda}\right]\int_{-\infty}^{\infty}e^{-y^2t-\lambda y}dy\,,$$

where $\lambda\equiv(2\pi ih)/d$. The integral is just $(\pi/t)^{1/2}\exp(\lambda^2/4t)$, so the sum on m becomes

$$\sum_m(s-md)e^{-(s-md)^2t}=-\frac{\sqrt{\pi}}{2d}\sum_h{}' e^{\lambda s}\lambda t^{-3/2}e^{\lambda^2/4t}$$
$$=-\frac{i\pi^{3/2}}{d^2}\sum_h{}' e^{2\pi ihs/d}ht^{-3/2}e^{-\pi^2h^2/d^2t}$$
$$=\frac{2\pi^{3/2}}{d^2}\sum_{h=1}^{\infty}t^{-3/2}h\sin\left[\frac{2\pi hs}{d}\right]e^{-\pi^2h^2/d^2t}\,.$$

The sum over m' is identical, and the double sum is just the product, i.e.,

$$\sum_{m,m'}(s-md)(s'-m'd')\exp[-(s-md)^2t-(s'-m'd')^2t]$$
$$=\frac{4\pi^3}{(dd')^2}\sum_{h,h'=1}^{\infty}t^{-3}hh'\sin\left[\frac{2\pi hs}{d}\right]\sin\left[\frac{2\pi h's'}{d}\right]\exp\left\{-\frac{\pi^2}{t}\left[\left[\frac{h}{d}\right]^2+\left[\frac{h'}{d'}\right]^2\right]\right\}.$$

Substitution of this expression into Eq. (14) and integration over t yields

$$\Sigma^{(n)}_{(\rho,s,s',d,d')}=\frac{8\pi^3}{\Gamma\left[\frac{n}{2}\right](dd')^2}\left[\frac{\pi}{\rho}\right]^{(n-6)/2}$$
$$\times\sum_{h,h'=1}^{\infty}hh'\sin\left[\frac{2\pi hs}{d}\right]\sin\left[\frac{2\pi h's'}{d'}\right]$$
$$\times\left[\left[\frac{h}{d}\right]^2+\left[\frac{h'}{d'}\right]^2\right]^{(n-6)/2}K_{(n-6)/2}\left[2\pi\rho\left[\left[\frac{h}{d}\right]^2+\left[\frac{h'}{d'}\right]^2\right]^{1/2}\right]. \quad (15)$$

The sums in Eqs. (12), (13), and (15) will converge rapidly because of the presence of the Bessel functions. The leading terms (with $h=0$) in the expressions for $\mathscr{S}^{(n)}$ and $S^{(n)}$ do not converge rapidly for small n as ρ increases, but these will be seen to cancel conveniently when the sums are used to evaluate the Lorentz factors.

4. *Special cases: $\rho=0$*

In transforming the sums in Eq. (7) into the expressions in Eqs. (12), (13), and (15), ρ was assumed greater than zero. However, the terms with $\rho=0$ will be needed to evaluate the Lorentz tensor components. For $\mathscr{S}^{(n)}$ and $S^{(n)}$ there are two possibilities if $\rho=0$: either $s=0$ or $s\neq 0$. For $\Sigma^{(n)}$ there are also two distinct possibilities if $\rho=0$: Either s and/or s' equals zero, or neither s nor s' equals zero. These four cases are considered separately in the following.

(a) Case 1: $\rho=0$, $s=0$. In this case the $m=0$ term must be excluded from each of the sums $\mathscr{S}^{(n)}$ and $S^{(n)}$. In the context of the dipole model, this is equivalent to excluding the dipole at the observation point. Because $\rho=0$ this case is equivalent to summing along an infinite chain of dipoles. Thus,

$$\mathscr{S}^{(n)}_{(0,0,d)}=\sum_m{}'\,|md|^{-n}$$
$$=2d^{-n}\sum_{m=1}^{\infty}m^{-n}$$
$$=2d^{-n}\zeta(n), \quad (16a)$$

$$S^{(n)}_{(0,0,d)}=\sum_m{}'\,|md|^{-(n-2)}$$
$$=2d^{-(n-2)}\zeta(n-2), \quad (16b)$$

where $\zeta(n)$ is the Riemann zeta function of n.

(b) Case 2: $\rho=0$, $s\neq 0$. For this case the $m=0$ term in each sum is retained (the observation point is not a lattice site). We have

$$\mathscr{S}^{(n)}_{(0,s,d)}=\sum_m|s-md|^{-n}$$
$$=d^{-n}\sum_{m=0}^{\infty}\left\{\left[m+\frac{s}{d}\right]^{-n}+\left[m+\left[1-\frac{s}{d}\right]\right]^{-n}\right\}, \quad (17a)$$

$$\mathscr{S}^{(n)}_{(0,s,d)}=d^{-n}\left[\zeta\left[n,\frac{s}{d}\right]+\zeta\left[n,1-\frac{s}{d}\right]\right],$$

$$S^{(n)}_{(0,s,d)}=d^{-(n-2)}\left[\zeta\left[n-2,\frac{s}{d}\right]+\zeta\left[n-2,1-\frac{s}{d}\right]\right], \quad (17b)$$

with $\zeta(n,s/d)$ the generalized Riemann zeta function. Note that, since $\zeta(n,1)=\zeta(n)$, cases 1 and 2 may be combined if $\zeta(n,0)$ is interpreted as $\zeta(n)$ by stipulating that the $m=0$ term is excluded from the sum if $s=0$.

(c) Case 3: $\rho=0$, s and/or $s'=0$. Inspection of

Eqs. (7c) and (15) indicates that $\Sigma^{(n)}=0$ if one or both of s and s' is zero, whether or not $\rho=0$, provided that the term $m=m'=0$ is excluded from the sum if $s=s'=0$. This will mean that the Lorentz tensor at a lattice site is diagonal.

(d) Case 4: $\rho=0$, $s\neq 0$, $s'\neq 0$. Equation (15) implies that $\Sigma^{(n)}=0$ if s and/or s' is equal to $\frac{1}{2}$, whether or not $\rho=0$. If neither s nor s' is equal to either 0 or $\frac{1}{2}$, the evident symmetry in Eq. (15) must be sacrificed in order to obtain a rapidly converging expression, i.e., only one of the indices may be summed over. Thus, for $\rho=0$, and neither s nor s' is equal to zero

$$\Sigma^{(n)}_{(0,s,s',d,d')}=\frac{1}{\Gamma\left[\frac{n}{2}\right]}\sum_{m'}(s'-m'd')\int_0^\infty t^{(n/2)-1}e^{-(s'-m'd')^2t}\left[\sum_m (s-md)e^{-(s-md)^2t}\right]dt$$

$$=\frac{4\pi^{3/2}}{d^2\Gamma\left[\frac{n}{2}\right]}\sum_{m'}(s'-m'd')\sum_{h=1}^{\infty}h\sin\left[\frac{2\pi hs}{d}\right]\int_0^\infty t^{(n-5)/2}\exp\left[-(s'-m'd')^2t-\frac{\pi^2h^2}{d^2t}\right]dt$$

$$=\frac{4\pi^{3/2}}{d^2\Gamma\left[\frac{n}{2}\right]}\sum_{m'}(s'-m'd')\sum_{h=1}^{\infty}h\sin\left[\frac{2\pi hs}{d}\right]\left[\frac{\pi h}{d\,|s'-m'd'|}\right]^{(n-3)/2}K_{(n-3)/2}\left[\frac{2\pi h\,|s'-m'd'|}{d}\right].$$

This may be rewritten as

$$\Sigma^{(n)}_{(0,s,s',d,d')}=\frac{4\pi^{3/2}}{d^2\Gamma\left[\frac{n}{2}\right]}(d')^{(-n-3)/2}\left\{\sum_{h=1}^{\infty}h\sin\left[\frac{2\pi hs}{d}\right]\left[\frac{\pi h}{d}\right]^{(n-3)/2}\right.$$

$$\times\sum_{m'=0}^{\infty}\left[\left[m'+\frac{s'}{d'}\right]^{-(n-5)/2}K_{(n-3)/2}\left[\frac{2\pi hd'}{d}\left[m'+\frac{s'}{d'}\right]\right]\right.$$

$$\left.\left.-\left[m'+1-\frac{s'}{d'}\right]^{(n-5)/2}K_{(n-3)/2}\left[\frac{2\pi hd'}{d}\left[m'+1-\frac{s'}{d'}\right]\right]\right]\right\}. \tag{18}$$

5. *Dipole sums*

The dipole sums required to evaluate the Lorentz tensor components are special cases of the generalized sums considered above. Reference to Eqs. (5) and (6) indicates that the required sums are $\mathscr{S}^{(3)}$, $S^{(5)}$, and $\Sigma^{(5)}$. Equations (12), (16a), and (17a) give for $\mathscr{S}^{(3)}$,

$$\mathscr{S}^{(3)}_{(\rho,s,d)}=d^{-3}\left[\zeta\left[3,\frac{s}{d}\right]+\zeta\left[3,1-\frac{s}{d}\right]\right]\delta_{\rho,0}+\frac{2}{d\rho^2}+\frac{4\pi}{d}\sum_h{}'e^{2\pi ihs/d}\left[\frac{|h|}{\rho d}\right]K_1\left[\frac{2\pi\,|h|\,\rho}{d}\right], \tag{19a}$$

where $\delta_{\rho,0}$ is the Kronecker delta function and the stipulation is made that $\zeta(3,0)$ is to be interpreted as $\zeta(3)$.

Similarly, Eqs. (13), (16b), and (17b) give $S^{(5)}$ as follows:

$$S^{(5)}_{(\rho,s,d)}=d^{-3}\left[\zeta\left[3,\frac{s}{d}\right]+\zeta\left[3,1-\frac{s}{d}\right]\right]\delta_{\rho,0}+\frac{2}{3d\rho^2}$$

$$+\frac{4\pi}{3d}\sum_h{}'e^{2\pi ihs/d}\left[\frac{|h|}{\rho d}K_1\left[\frac{2\pi\,|h|\,\rho}{d}\right]-2\pi\left[\frac{h}{d}\right]^2K_0\left[\frac{2\pi\,|h|\,\rho}{d}\right]\right], \tag{19b}$$

with the same stipulation on the meaning of $\zeta(3,0)$.

Two different expressions for $\Sigma^{(5)}$ must be given. The more general one, which can be used in all cases except special case 4 above, is obtained from Eq. (15) as follows:

$$\Sigma^{(5)}_{(\rho,s,s',d,d')}=\frac{32\pi^2}{(dd')^2}\rho^{1/2}\sum_{h,h'=0}^{\infty}hh'\sin\left[\frac{2\pi hs}{2}\right]\sin\left[\frac{2\pi h's'}{d'}\right]$$
$$\times\left[\left[\frac{h}{d}\right]^2+\left[\frac{h'}{d'}\right]^2\right]^{-1/4}K_{1/2}\left[2\pi\rho\left[\left[\frac{h}{d}\right]^2+\left[\frac{h'}{d'}\right]^2\right]^{1/2}\right], \tag{20a}$$

where the fact that $K_{-\nu}(z)=K_\nu(z)$ has been used. For the special case in which $\rho=0$ and neither s nor s' equals zero, Eq. (18) gives

$$\Sigma^{(5)}_{(0,s,s',d,d')}=\frac{16\pi^2}{3d^3}\sum_{h=1}^{\infty}\left\{h^2\sin\left[\frac{2\pi hs}{d}\right]\sum_{m'=0}^{\infty}\left[K_1\left[\frac{2\pi hd'}{d}\left[m'+\frac{s'}{d'}\right]\right]\right.\right.$$
$$\left.\left.-K_1\left[\frac{2\pi hd'}{d}\left[m'+1-\frac{s'}{d'}\right]\right]\right]\right\}. \tag{20b}$$

C. Lorentz tensor components

Obtaining expressions for the Lorentz tensor components is now a simple matter of associating the arguments of the dipole sums with the appropriate arguments of a desired tensor component. For example, Eq. (5) indicates that, to obtain the Lorentz factor L_{cc}, the infinite sum is over the index j, which is associated with lattice spacing c and observation point coordinate x. Comparison of Eqs. (5) and (7) then allows L_{cc} to be written

$$L_{cc}(c,a,b,x,y,z)=\frac{abc}{4\pi}\sum_{k,l}(3S^{(5)}_{(\rho_{ab},x,c)}-\mathscr{S}^{(3)}_{(\rho_{ab},x,c)}),$$

with $\rho_{ab}=[(y-ka)^2+(z-lb)^2]^{-1/2}$. Here the full functional dependence of L_{cc} has been indicated explicitly, to emphasize that the Lorentz factors depend on both the lattice spacings and the observation point coordinates. With Eqs. (19a) and (19b), the expression for L_{cc} becomes

$$L_{cc}(c,a,b,x,y,z)=\frac{1}{2\pi}\frac{ab}{c^2}\left[\zeta\left[3,\frac{x}{c}\right]+\zeta\left[3,1-\frac{x}{c}\right]\right]\delta_{\rho_{ab},0}-2\pi\frac{ab}{c^2}\sum_{k,l}{}'\sum_{h}e^{2\pi ihx/c}h^2K_0\left[\frac{2\pi\,|\,h\,|\,\rho_{ab}}{c}\right], \tag{21a}$$

where the sum over k and l excludes the term having $k=l=0$ if y and z are both zero, and includes it otherwise. The other two Lorentz factors L_{aa} and L_{bb} will be of the same form, with appropriate interchanges of lattice spacings and observation point coordinates. It can be seen from Eq. (21a) that the Lorentz factors do not depend on the absolute magnitudes of the lattice spacings and observation point coordinates, but rather on ratios among c, a, and b and ratios x/c, y/a, and z/b. This is more evident if the argument of the Bessel function is rewritten as follows:

$$\frac{2\pi\,|\,h\,|\,\rho_{ab}}{c}=2\pi\,|\,h\,|\left[\left[\frac{y}{a}-k\right]^2\left[\frac{a}{c}\right]^2+\left[\frac{z}{b}-l\right]^2\left[\frac{b}{c}\right]^2\right]^{1/2}.$$

Thus the Lorentz factors are completely specified by two ratios among the lattice spacings and the fractional distance of the observation point from a lattice site. It will be convenient to define an ordered triplet $\vec{f}=(f_c,f_a,f_b)$ whose components are the fractional observation point distances, i.e., $f_c=x/c$, $f_a=y/a$, $f_b=z/b$. Then Eq. (21a) may be written

$$L_{cc}(c,a,b,f_c,f_a,f_b)=\frac{1}{2\pi}\frac{ab}{c^2}[\zeta(3,f_c)+\zeta(3,1-f_c)]\delta_{\rho_{ab},0}-2\pi\frac{ab}{c^2}\sum_{k,l}\sum_{h}{}' e^{2\pi i h f_c}h^2K_0\left[\frac{2\pi\,|\,h\,|\rho_{ab}}{c}\right] . \tag{21b}$$

Another symmetry is evident from these expressions: The Lorentz factor associated with a particular axis is symmetric with respect to interchanges of all variables associated with the other two axes. For example, L_{cc} is unchanged if a is interchanged with b and f_a with f_b as follows:

$$L_{cc}(c,a,b,f_c,f_a,f_b)=L_{cc}(c,b,a,f_c,f_b,f_a) .$$

Expressions for the off-diagonal Lorentz tensor components are obtained in a similar fashion, by identifying appropriate lattice spacings and observation point coordinates with the arguments of $\Sigma^{(5)}$. For example, Eq. (6) indicates that to obtain L_{ca}, the infinite sums are over indices j and k, associated with lattice spacings c and a. Comparison of Eqs. (6) and (7c) then indicates that L_{ca} can be written in terms of $\Sigma^{(5)}(\,|\,z-lb\,|\,,x,y,c,a)$. The most general expression for L_{ca} is given by

$$L_{ca}(c,a,b,x,y,z)=\frac{3abc}{4\pi}\left[\delta_{z,0}\Sigma^{(5)}(0,x,y,c,a)+\sum_{l}\Sigma^{(5)}(\,|\,z-lb\,|\,,x,y,c,a)\right] , \tag{22a}$$

where $\delta_{z,0}$ is the Kronecker delta function, and the sum over l excludes the term $l=0$ if z is equal to zero. The expression for $\Sigma^{(5)}(0,x,y,c,a)$ is obtained from Eq. (20b) while that for $\Sigma^{(5)}(\,|\,z-lb\,|\,,x,y,c,a)$ is obtained from Eq. (20a). Like the Lorentz factors, the off-diagonal components of the tensor are functions of ratios among the lattice spacings and the f_i defined above. Then, if $z\neq 0$, L_{ca} is given by

$$\begin{aligned}L_{ca}&(c,a,b,f_c,f_a,f_b)\\&=\frac{24\pi b^2}{2c}\sum_{l}\left\{|\,f_b-l\,|^{1/2}\sum_{h,h'=1}^{\infty}hh'\sin(2\pi hf_c)\sin(2\pi h'f_a)\right.\\&\qquad\left.\times\left[\left[\frac{hb}{c}\right]^2+\left[\frac{h'b}{a}\right]^2\right]^{1/4}K_{1/2}\left[2\pi\,|\,f_b-l\,|\,\left[\left[\frac{hb}{c}\right]^2+\left[\frac{h'b}{a}\right]^2\right]^{1/2}\right]\right\} ,\end{aligned} \tag{22b}$$

and if $z=0$, it is

$$\begin{aligned}L_{ca}(c,a,b,f_c,f_a,0)=&\frac{4\pi ab}{c}\sum_{h=1}^{\infty}\left\{h^2\sin(2\pi hf_c)\sum_{m=0}^{\infty}\left[K_1\left[\frac{2\pi ha}{c}(m+f_a)\right]-K_1\left[\frac{2\pi ha}{c}(m+1-f_a)\right]\right]\right\}\\&+\frac{24\pi b^2}{ac}\sum_{l}{}'\left[|\,l\,|^{1/2}\sum_{h,h'=1}^{\infty}hh'\sin(2\pi hf_c)\sin(2\pi h'f_a)\right.\\&\qquad\times\left[\left[\frac{hb}{c}\right]^2+\left[\frac{h'b}{a}\right]^2\right]^{-1/4}\\&\qquad\left.\times K_{1/2}\left\{2\pi\,|\,f_b-l\,|\,\left[\left[\frac{hb}{c}\right]^2+\left[\frac{h'b}{a}\right]^2\right]^{1/2}\right\}\right] .\end{aligned} \tag{22c}$$

Similar expressions may be obtained for the other off-diagonal elements. The fact that $\Sigma^{(5)}(\rho,s,s',d,d')=0$ if either s and/or s' is zero or $\frac{1}{2}$ means that the Lorentz tensor is diagonal if any two of f_c,f_a,f_b have any combination of these values.

D. Derivatives of Lorentz factors

Derivatives of the Lorentz factors with respect to the lattice spacings are of interest because they will arise in theories describing physical processes in which small deformations of the lattice occur such as piezoelectricity and pyroelectricity. They can be readily obtained from Eqs. (5) and (21), and the analogous expressions for L_{aa} and L_{bb}. The resulting expressions provide some useful relationships among the derivatives, provided that $\vec{f}$ is held constant.

From the sum rule for the Lorentz factors in Eq. (4), i.e.,

$$L_{cc}(c,a,b,\vec{f})+L_{aa}(c,a,b,\vec{f})+L_{bb}(c,a,b,\vec{f})=1 ,$$

in which $\vec{f}$ stands for the ordered triplet (f_c,f_a,f_b), it follows that

$$\begin{aligned}
&\left[\frac{\partial L_{cc}}{\partial a}\right]_{b,c,\vec{f}}+\left[\frac{\partial L_{aa}}{\partial a}\right]_{b,c,\vec{f}}+\left[\frac{\partial L_{bb}}{\partial a}\right]_{b,c,\vec{f}}=0 ,\\
&\left[\frac{\partial L_{cc}}{\partial b}\right]_{a,c,\vec{f}}+\left[\frac{\partial L_{aa}}{\partial b}\right]_{a,c,\vec{f}}+\left[\frac{\partial L_{bb}}{\partial b}\right]_{a,c,\vec{f}}=0 ,\\
&\left[\frac{\partial L_{cc}}{\partial c}\right]_{a,b,\vec{f}}+\left[\frac{\partial L_{aa}}{\partial c}\right]_{a,b,\vec{f}}+\left[\frac{\partial L_{bb}}{\partial c}\right]_{a,b,\vec{f}}=0 ,
\end{aligned} \tag{23}$$

where the subscripts outside the parentheses indicate the variables being held constant and the arguments of the Lorentz factors have been suppressed for notational simplicity.

A second sum rule applies for each Lorentz factor, i.e.,

$$\left[\frac{\partial L_{ll}}{\partial(\ln a)}\right]_{b,c,\vec{f}}+\left[\frac{\partial L_{ll}}{\partial(\ln b)}\right]_{a,c,\vec{f}}+\left[\frac{\partial L_{ll}}{\partial(\ln c)}\right]_{a,b,\vec{f}}=0 , \tag{24}$$

where ll may take on values aa,bb,cc. Because all three Lorentz factors are of the same form, Eq. (24) is proved for all three if demonstrated for one. This is done below using Eq. (21b) for L_{cc}. The derivatives are

$$\begin{aligned}
\left[\frac{\partial L_{cc}}{\partial(\ln a)}\right]_{b,c,\vec{f}}&=\frac{1}{2\pi}\frac{ab}{c^2}[\zeta(3,f_c)+\zeta(3,1-f_c)]\delta_{\rho_{ab},0}-\frac{2\pi ab}{c^2}\\
&\quad\times\sum_{j,k}\sum_{h}{}'e^{2\pi i h f_c}h^2\left[K_0\left[\frac{2\pi|h|\rho_{ab}}{c}\right]+a\frac{\partial}{\partial a}K_0\left[\frac{2\pi|h|\rho_{ab}}{c}\right]\right] ,\\
\left[\frac{\partial L_{cc}}{\partial(\ln a)}\right]_{b,c,\vec{f}}&=L_{cc}+\frac{4\pi^2 ab}{c^3}\sum_{k,l}\sum_{h}{}'e^{2\pi i h f_c}|h|^3(f_a-k)^2a^2\rho_{ab}^{-1}K_1\left[\frac{2\pi|h|\rho_{ab}}{c}\right] ,
\end{aligned} \tag{25a}$$

$$\left[\frac{\partial L_{cc}}{\partial(\ln b)}\right]_{a,c,\vec{f}}=L_{cc}+\frac{4\pi^2 ab}{c^3}\sum_{k,l}\sum_{h}{}'e^{2\pi i h f_c}|h|^3(f_b-l)^2b^2\rho_{ab}^{-1}K_1\left[\frac{2\pi|h|\rho_{ab}}{c}\right] , \tag{25b}$$

$$\left[\frac{\partial L_{cc}}{\partial(\ln c)}\right]_{a,b,\vec{f}}=L_{cc}+\frac{4\pi^2 ab}{c^3}\sum_{k,l}\sum_{h}{}'e^{2\pi i h f_c}|h|^3\rho_{ab}K_1\left[\frac{2\pi|h|\rho_{ab}}{c}\right] . \tag{25c}$$

Adding these three equations yields

$$\begin{aligned}
&\left[\frac{\partial L_{cc}}{\partial(\ln a)}\right]_{b,c,\vec{f}}+\left[\frac{\partial L_{cc}}{\partial(\ln b)}\right]_{a,c,\vec{f}}+\left[\frac{\partial L_{cc}}{\partial(\ln c)}\right]_{a,b,\vec{f}}\\
&=\frac{4\pi^2 ab}{c^3}\sum_{k,l}\sum_{h}{}'\left[e^{2\pi i h f_c}|h|^3\{[(f_a-k)^2a^2+(f_b-l)^2b^2]\rho_{ab}^{-1}-\rho_{ab}\}K_1\left[\frac{2\pi|h|\rho_{ab}}{c}\right]\right]=0 ,
\end{aligned}$$

the term in braces vanishing by definition of ρ_{ab}. This proves Eq. (24).

Equations (23) and (24) are in a sense the same statement, because the derivatives of the Lorentz factors are interrelated by

$$\left[\frac{\partial L_{cc}}{\partial(\ln a)}\right]_{b,c,\vec{f}}=\left[\frac{\partial L_{aa}}{\partial(\ln c)}\right]_{a,b,\vec{f}},$$
$$\left[\frac{\partial L_{cc}}{\partial(\ln b)}\right]_{a,c,\vec{f}}=\left[\frac{\partial L_{bb}}{\partial(\ln c)}\right]_{a,b,\vec{f}}, \quad (26)$$
$$\left[\frac{\partial L_{aa}}{\partial(\ln b)}\right]_{a,c,\vec{f}}=\left[\frac{\partial L_{bb}}{\partial(\ln a)}\right]_{b,c,\vec{f}}.$$

This is shown in the most straightforward fashion by taking derivatives on Eq. (5) and its analogs for L_{aa} and L_{bb}, and comparing appropriate pairs of derivatives.

Evidently, if $f_c=0$, the sums appearing in Eqs. (25a)–(25c) are positive definite. The analogous sums in the expressions for the derivatives of L_{aa} and L_{bb} will be positive definite if $f_a=0$ and $f_b=0$, respectively. Because of this, the relations in Eq. (26), and the sum rule for the Lorentz factors in Eq. (4), if $f_a=f_b=f_c=0$,

$$\frac{\partial L_{ll}}{\partial(\ln k)}-L_{ll}>0, \quad k\neq 1$$
$$\frac{\partial L_{ll}}{\partial(\ln l)}-L_{ll}<0, \quad (27)$$

where k and l take on values a,b,c, and the partial derivatives are taken holding all variables except the lattice spacing indicated in the denominator constant, as in Eq. (26). The condition $\vec{f}=0$ applies when the Lorentz factor is computed for a lattice site of a simple orthorhombic lattice.

E. Application to orthorhombic lattices

In this section the expressions developed in the foregoing are used to examine the dependence of Lorentz factors at lattice sites on lattice spacing for the cases of body-centered and base-centered orthorhombic lattices. These may be obtained by envisioning the lattice to be composed of two interlocking simple sublattices and superimposing the dipole fields.

Equations (1) and (3) indicate the dipole field at point $\vec{r}$ inside an ellipsoidal crystal with uniform polarization $\vec{P}$ is given by

$$\vec{E}_{\rm dip}(\vec{r})=\frac{\alpha_0}{\epsilon_0}[\vec{L}(\vec{r})-\tilde{D}]\vec{P}, \quad (28)$$

where use has been made of the fact that the depolarization tensor is constant throughout the volume of a uniformly polarized ellipsoid. The field at a lattice site of a body- or base-centered orthorhombic crystal can be found by superimposing the fields from two identical interlocking sublattices such as those illustrated in Fig. 2. The Lorentz tensor components desired are those appropriate to a lattice site of the A sublattice. The total diple field at such a site is

$$\vec{E}_{\rm dip}(\vec{0}_A)=\vec{E}_{{\rm dip}AA}(\vec{0})+\vec{E}_{{\rm dip}AB}(\vec{r}_{AB}),$$

where $(\vec{0}_A)$ indicates that this is the field at an A sublattice site, $\vec{E}_{{\rm dip}AA}(\vec{0})$ is the field due to the dipoles on the A sublattice at its own lattice site, $\vec{E}_{{\rm dip}AB}(\vec{r}_{AB})$ is the field due to dipoles on the B sublattice at an A lattice site, and $\vec{r}_{AB}$ is a vector locating the A lattice site in the unit cell of the B sublattice. The sublattices have lattice spacings c,a,b in $\hat{x},\hat{y},\hat{z}$, respectively. With $\vec{f}_{AB}$ defined as $\vec{r}_{AB}$ normalized to the lattice spacings as before,

$$\vec{E}_{{\rm dip}AA}(\vec{0})=\frac{\alpha_0}{\epsilon_0}[\tilde{L}(c,a,b,\vec{0})-\tilde{D}]\vec{P}_A,$$

$$\vec{E}_{{\rm dip}AB}(\vec{r}_{AB})=\frac{\alpha_0}{\epsilon_0}[\tilde{L}(c,a,b,\vec{f}_{AB})-\tilde{D}]\vec{P}_B,$$

where $\tilde{D}$ is the same in both cases because the two imagined sublattices are macroscopically identical. If $\vec{P}_A=\vec{P}_B$, the total polarization is $\vec{P}=\vec{P}_A+\vec{P}_B=2\vec{P}_A$, whence

$$\vec{E}_{\rm dip}(\vec{0}_A)=\frac{\alpha_0}{\epsilon_0}\{\tfrac{1}{2}[\tilde{L}(c,a,b,\vec{0})+\tilde{L}(c,a,b,\vec{f}_{AB})]-\tilde{D}\}\vec{P}. \quad (29)$$

Comparison of this expression to Eq. (28) indicates that the Lorentz tensor for the whole lattice is

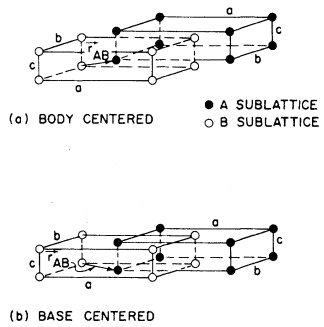

FIG. 2. Identical interlocking sublattice used to find Lorentz factors for orthorhombic lattices. (a) Body centered. (b) Base centered.

$$\tilde{L}=\tfrac{1}{2}[\tilde{L}(c,a,b,\vec{0})+\tilde{L}(c,a,b,\vec{f}_{AB})] . \quad (30)$$

The field at an A lattice site for $\vec{P}_A \neq \vec{P}_B$ is given by

$$\vec{E}_{\rm dip}(\vec{0}_A)=\frac{\alpha_0}{\epsilon_0}[\tilde{L}(c,a,b,\vec{0})\vec{P}_A + \tilde{L}(c,a,b,\vec{f}_{AB})\vec{P}_B-\tilde{D}\vec{P}] .$$

From this expression it is clear that, even for the case of an antiferroelectric substance in which $\vec{P}_B=-\vec{P}_A$, the dipole field at a lattice site is not, in general, zero, even though the total polarization is zero.

For the body-centered and base-centered orthorhombic structures depicted in Fig. 2, the fractional offsets are

$$\vec{f}_{AB}^{\,(\rm body)}=(\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}) ,$$
$$\vec{f}_{AB}^{\,(\rm base)}=(0,\tfrac{1}{2},\tfrac{1}{2}) ,$$

where the choice of the $\hat{x}$ (or c) direction in the base-centered case is, to this point, arbitrary. For these values of $\vec{f}_{AB}$, the Lorentz tensor is diagonal, and the field is completely specified by the three Lorentz factors for each case under consideration. The Lorentz factors for the body-centered lattice are given by

$$L_l^{(\rm body)}=\tfrac{1}{2}(L_{AAl}+L_{ABl}^{(\rm body)}) \quad (31a)$$

and those for the base-centered case by

$$L_l^{(\rm base)}=\tfrac{1}{2}(L_{AAl}+L_{ABl}^{(\rm base)}) \quad (31b)$$

where l takes on the values a,b,c and

$$L_{AAl}\equiv L_{ll}(c,a,b,\vec{0}) ,$$
$$L_{ABl}^{(\rm body)}\equiv L_{ll}(c,a,b,\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}) ,$$
$$L_{ABl}^{(\rm base)}\equiv L_{ll}(c,a,b,0,\tfrac{1}{2},\tfrac{1}{2}) ,$$

have been defined to simplify the notation.

Because the Lorentz factors depend only on ratios among the lattice spacings, their dependence on structure can be examined by specifying $a\geq b\geq c$ and computing the Lorentz factors as functions of b/a and c/b as these ratios vary from zero to one. The choice of $a\geq b\geq c$ means that, for the base-centered case, the zero shift between sublattices is in the short axis. This choice was motivated by interest in future applications of the model.

From the expressions in Eq. (31), it can be seen that the contributions to the Lorentz factors for both base- and body-centered cases due to the A sublattice are the same. They are just the Lorentz factors at a lattice site of a simple orthorhombic crystal, which have been tabulated by Colpa.[1] Their values were computed using the expressions derived in the preceding section. Results agreed with Colpa's to the accuracy of the present calculation (four places after the decimal). It should be noted that he has used $c\geq b\geq a$, so a and c must be interchanged for the comparison. These results are plotted in Fig. 3, for comparison to contributions from the B sublattice. Calculations of the Lorentz factors were made at intervals of 0.1 in b/a and c/b, and the curves drawn through the points. In the plots, the three Lorentz factors are shown as functions of the intermediate-to-long lattice-constant ratio (b/a) for various values of the short-to-intermediate lattice-constant ratio (c/b). The term "axis" in the figure captions is borrowed from Colpa's terminology. However, it is not meant to imply any macroscopic shape, but only to indicate the direction corresponding to a particular lattice spacing. Thus the long axis is the $\hat{y}$ direction in which the largest lattice spacing (a) has been assumed here. The $\hat{z}$ (b) and $\hat{x}$ (c) directions are the intermediate and short axes, respectively.

It is immediately clear from Fig. 3 that the Lorentz factors for the long and intermediate axes are negative for substantial ranges of $(b/a,c/b)$. This observation has been made before,[1,8] but is worth emphasizing because it implies that the internal electric field in these directions will tend to reduce the moments of molecules in the lattice rather than enhance them. That is, negative Lorentz factors imply depolarizing internal field components. The Lorentz factor for the short axes, L_{AAc}, shown as broken lines in Fig. 3(b), is always

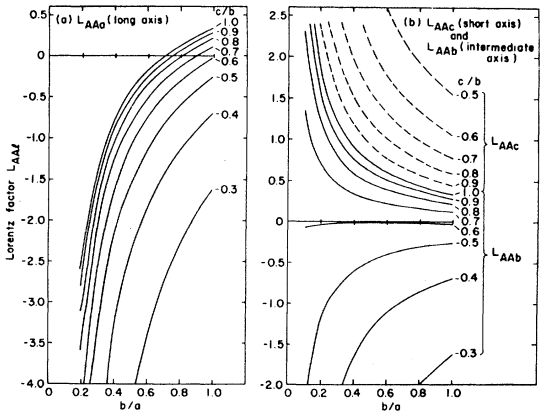

FIG. 3. Lorentz factors for lattice site of simple orthorhombic lattice (sublattice A). (a) L_{AAa} (long axis). (b) L_{AAc} (short axis) and L_{AAb} (intermediate axis).

positive (polarizing) and becomes strongly so for small values of c/b and b/a. The lines labeled $c/b=1$ in Fig. 3 give the Lorentz factors for a tetragonal lattice whose two equal unit-cell dimensions are shorter than the third. Along this line in Fig. 3(b) $L_{AAb}=L_{AAc}$. When $b/a=c/b=1$, the lattice is cubic and each Lorentz factor has the value $\frac{1}{3}$ as is required by symmetry.

The Lorentz factors $L_{ABl}^{(\text{body})}$ are plotted in Fig. 4. In contrast to the A sublattice factors, these are always positive and in the range $0 \leq L_{ABl}^{(\text{body})} \leq 1$. Thus, the B lattice never contributes a depolarizing field in the body-centered lattice. However, for small values of b/a or c/b, the field due to dipoles on the A sublattice will dominate. When $b/a=c/b=1$, the point at which $L_{ABl}^{(\text{body})}$ is calculated has cubic symmetry, so that all three Lorentz factors are equal to $\frac{1}{3}$.

Lorentz factors for body-centered orthorhombic lattices, calculated using Eq. (31a) are shown in Fig. 5. As anticipated, the range of geometries for which the Lorentz factors for the long and intermediate axes are negative is smaller than for the simple orthorhombic lattice. But a large range of $(b/a, c/b)$ values still yield negative Lorentz factors, i.e., depolarizing fields. This is illustrated in the diagrams in Fig. 6, in which the signs of the Lorentz factors in the long and intermediate axes are indicated as regions in c/b-b/a space for simple and

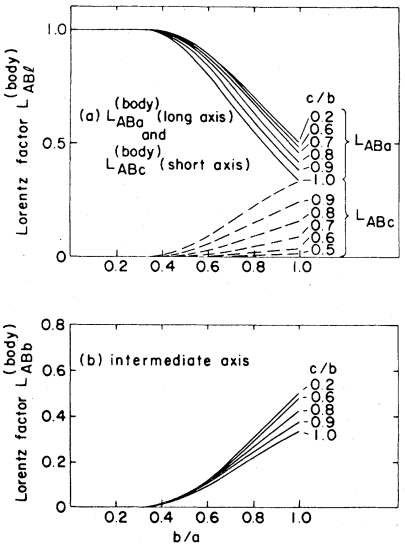

FIG. 4. Lorentz factors at lattice site of A due to dipoles of B, body-centered case. (a) $L_{ABa}^{(\text{body})}$ (long axis) and $L_{ABc}^{(\text{body})}$ (short axis). (b) Intermediate axis.

body-centered orthorhombic lattices.

Figure 7 shows the Lorentz factors $L_{ABl}^{(\text{base})}$ for the case of zero shift in the short axis. The magnitude of these factors range from zero to one, as was the case for the body-centered B sublattice factors. However, for the base-centered case, the short axis factor $L_{ABC}^{(\text{base})}$ is less than or equal to zero for all

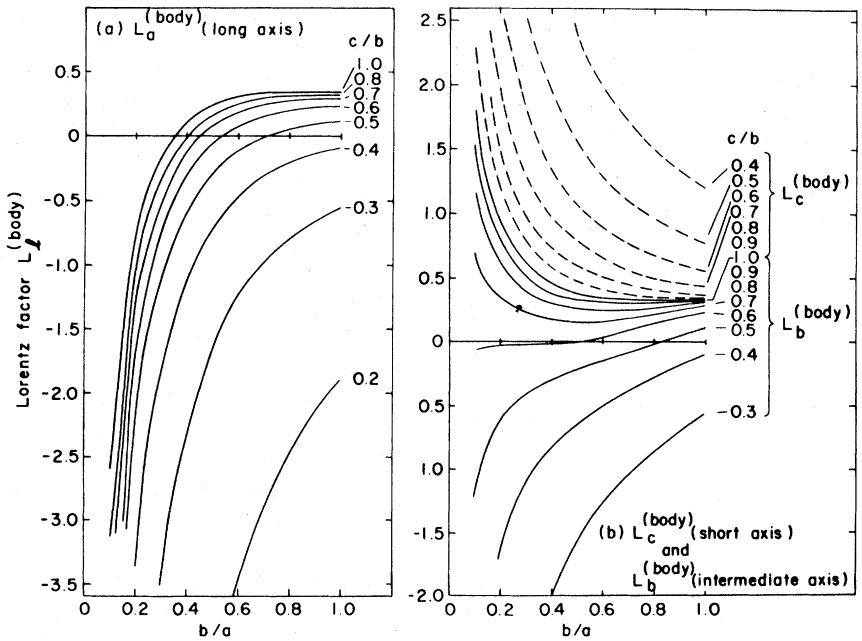

FIG. 5. Lorentz factors for lattice site of body-centered orthorhombic lattice. (a) $L_a^{(\text{body})}$ (long axis). (b) $L_c^{(\text{body})}$ (short axis) and $L_b^{(\text{body})}$ (intermediate axis).

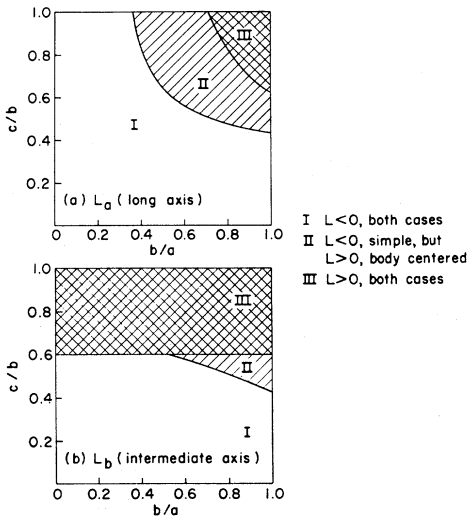

FIG. 6. Geometries yielding polarizing ($L>0$) and depolarizing ($L<0$) fields for simple and body-centered orthorhombic lattices. (a) L_a (long axis). (b) L_b (intermediate axis).

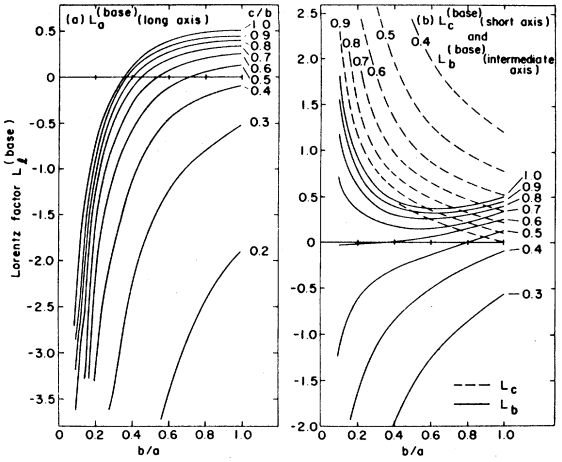

FIG. 8. Lorentz factors for lattice site of base-centered orthorhombic lattice as functions of b/a for various values of c/b. (a) $L_a^{(base)}$ (long axis). (b) $L_c^{(base)}$ (short axis) and $L_b^{(base)}$ (intermediate axis).

(b/a,c/b) combinations. The A lattice site at which the Lorentz factors are being computed is no longer a point of cubic symmetry when $b/a=c/b=1$, and this is reflected in the inequality of the Lorentz factors in this case.

Lorentz factors for base-centered orthorhombic lattices, computed according to Eq. (31b), are plotted in Fig. 8. The factors $L_a^{(base)}$ and $L_b^{(base)}$ are similar to their counterparts for the body-centered case (Fig. 5). The short-axis Lorentz factor $L_c^{(base)}$, however, has been shifted down by the negative contributions from $L_{ABC}^{(base)}$, and is less than $L_b^{(base)}$ and $L_a^{(base)}$ for a range of (b/a,c/b) values. Thus, while $L_c^{(body)} \geq L_b^{(body)} \geq L_a^{(body)}$ and $L_{AAc} \geq L_{AAb}$ $\geq L_{AAa}$ for any particular (b/a,c/b) value, this is not the case for the base-centered lattice.

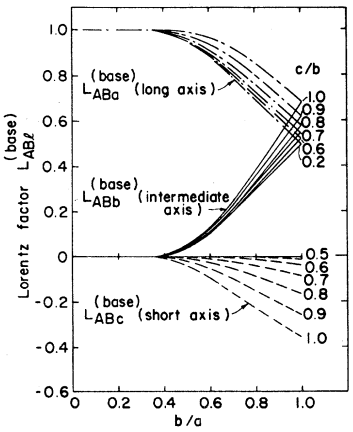

FIG. 7. Lorentz factors at lattice site of A due to dipoles of B, base-centered in a-b plane.

Derivatives of the Lorentz factors with respect to lattice dimensions are of importance in processes involving responses of strained crystals. Mueller[8] has discussed their importance to the photoelastic effect in cubic crystals. He gives values for the derivations of L_c and L_b for a cubic lattice deformed in the z (b) direction, and compares them to values found using two derivations different from his own. The results he quotes are given in Table I along with values found using the method described here, for comparison.

To illustrate the variation of the derivatives with lattice geometry, the nine logarithmic derivatives of the Lorentz factors at a lattice site of a simple orthorhombic lattice (sublattice A), i.e.,

$$\left[\frac{\partial L_{AAl}}{\partial(\ln k)}\right], \quad k,l=a,b,c \ .$$

were computed. These logarithmic derivatives of the Lorentz factors, like the factors themselves, are functions of ratios among the lattice spacings and therefore may be displayed in the same form as were the factors, i.e., as functions of b/a for various values of c/b with $a \geq b \geq c$. Each of the nine derivatives was calculated for each (b/a, c/b) value. Results satisfied the relations given in Eqs. (23), (24), and (26) to four places beyond the decimal point in every case. Computations were made at intervals of 0.1 in b/a and 0.2 in c/b. The lines

TABLE I. Derivatives of Lorentz factors for a cubic lattice strained in $\hat{z}$ (b) direction.

$\frac{\partial L_c}{\partial b}$	$\frac{\partial L_b}{\partial b}$	Source
0.499	−1.000	Mueller,[a] his own method
0.501	−1.01	Herzfeld, quoted by Mueller[a]
0.5045	−1.0090	Mueller, using Banerjee's method[a]
0.5049	−1.0098	Present method

[a]Reference 8.

shown in Fig. 9 were drawn through the points to illustrate the variation of the derivatives with lattice geometry. From Fig. 9 it can be seen that the derivative of a Lorentz factor with respect to the lattice parameter whose axis is associated with it, e.g., $(\partial L_{AAa}/\partial lna)$, is always negative while those with respect to the other lattice parameters may be of either sign. At least one must be positive, in consequence of Eq. (24).

It is clear from the foregoing that both the Lorentz factors and their derivatives for orthorhombic lattices are strongly dependent on lattice structure. They may take on any value, positive or negative. Therefore, use of the usual classical theory of dielectrics, which assumes the validity of the Lorentz field approximation, effectively setting each of the Lorentz factors equal to $\frac{1}{3}$ and their derivatives equal to zero can lead to large errors for noncubic crystals.

III. POLARIZABLE MOLECULES

The internal electric field at a lattice site of a crystal of point dipoles is a strong function of lattice geometry. If the dipoles are associated with polarizable molecules, the polarization state of the crystal will be structure dependent. Thus if there is some dipole moment associated with a "bare" molecule, this moment will be modified in the crystalline environment by an amount which is structure dependent. If the molecules have no permanent moment, the structure will influence the polarization developed under a given applied field. When the crystal is strained, the internal field changes, and the polarization, if any, changes also.

In this section a uniformly polarized crystal of polarizable point dipoles on an orthorhombic lattice is considered. To simplify the notation, the crystal is imagined to be an ellipsoid with at least one of its principal axes coinciding with a lattice vector (Lorentz direction). The applied field due to external sources and any permanent moment of the molecules in the lattice are presumed to be in the same direction as this common axis. With these assumptions, the tensor notation may be suppressed. The local electric field $E_{\rm loc}$ acting on a molecule (at a lattice site) is given by

$$E_{\rm loc}=E_{\rm appl}+\frac{\alpha_0}{\epsilon_0}(L-D)P\ ,$$

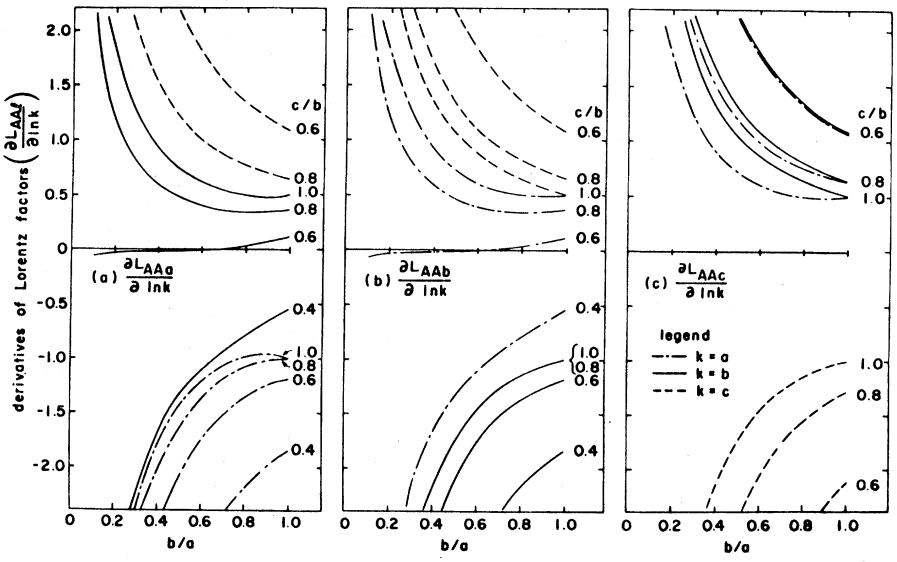

FIG. 9. Logarithmic derivatives of Lorentz factors for simple orthorhombic lattice. (a) $\partial L_{AAa}/\partial lnk$. (b) $\partial L_{AAb}/\partial lnk$. (c) $\partial L_{AAc}/\partial lnk$.

where E_{appl} is the applied field due to external sources and L is the Lorentz factor for the common axis. It is convenient to define a macroscopic field in the medium E_{med} as the sum of the applied and depolarization fields,[1]

$$E_{\text{med}}=E_{\text{appl}}-\frac{\alpha_0}{\epsilon_0}DP ,$$

whence

$$E_{\text{loc}}=E_{\text{med}}+\frac{\alpha_0}{\epsilon_0}LP . \tag{32}$$

We first suppose the molecules to have no permanent dipole moment, but to have molecular polarizability α. The induced dipole moment p is related to α by

$$p=\alpha E_{\text{loc}}$$

and, if all the molecules are the same, the polarization is just $P=np$, with n the number of dipoles per unit volume. Then, from Eq. (32),

$$P=n\alpha\left[E_{\text{med}}+\frac{\alpha_0}{\epsilon_0}LP\right] . \tag{33}$$

The polarization is related to the macroscopic field E_{med} through the dielectric constant κ by

$$\frac{P}{E_{\text{med}}}=\frac{\epsilon_0}{\alpha_0}(\kappa-1) ,$$

which, with Eq. (33), allows $n\alpha$ to be expressed in terms of κ as

$$n\alpha=\frac{\epsilon_0}{\alpha_0}\left[\frac{\kappa-1}{1+(\kappa-1)}\right] . \tag{34}$$

Note that for the case of cubic symmetry, i.e., when $L=\frac{1}{3}$, this reduces to the usual Clausius-Mossotti relation,

$$n\alpha=\frac{\epsilon_0}{\alpha_0}\left[\frac{3(\kappa-1)}{\kappa+2}\right] .$$

Now suppose the molecules to have permanent moments p_0. Then the moment of each molecule is

$$p=p_0+\alpha E_{\text{loc}} ,$$

or, in terms of the polarization,

$$P=P_0+n\alpha E_{\text{loc}} , \tag{35}$$

where $P_0=np_0$. With E_{loc} as defined in Eq. (32), and Eq. (34) relating $n\alpha$ to κ and L, Eq. (35) becomes

$$P=[1+L(\kappa-1)]P_0+\frac{\epsilon_0}{\alpha_0}(\kappa-1)E_{\text{med}} . \tag{36}$$

Then, if it is arranged to have $E_{\text{med}}=0$,

$$P=[1+L(\kappa-1)]P_0 , \tag{37}$$

which, for $L=\frac{1}{3}$ becomes $P=(\frac{1}{3})(\kappa+2)P_0$, the enhancement due to self-polarization found using the Lorentz field approximation. It may be noted that Eqs. (36) and (37) hold for each component of P and E_{med} if all the tensors (L, κ, and α) are diagonal. The appropriate dielectric constant κ is the electronic or high-frequency one, sometimes called κ_∞ and associated with the index of refraction.

In Sec. II it was found that many choices of lattice dimensions result in one or two negative Lorentz factors. Because $\kappa\geq 1$ in all cases, Eq. (37) implies that the "enhancement" due to self-polarization will actually be a reduction in these directions, i.e., P will be less than P_0 for crystal axes having negative Lorentz factors.

Equation (34) may be solved for $(\kappa-1)$ to find

$$(\kappa-1)=\frac{\frac{\alpha_0}{\epsilon_0}n\alpha}{1-\frac{\alpha_0}{\epsilon_0}n\alpha L} . \tag{38}$$

This indicates that if the molecular polarizability α is isotropic, the dielectric constant κ will be anisotropic for noncubic crystals. Equation (38) also implies the possibility of a structure-dependent "polarization catastrophe," i.e., a finite value of P with $P_0=E_{\text{med}}=0$, or equivalently, $\kappa\to\infty$, when $L=\epsilon_0/(\alpha_0 n\alpha)$.

IV. CONCLUSION

The electric field internal to a crystal of molecular dipoles depends on the lattice structure through the Lorentz tensor. While this tensor is in general different from the dipole sum tensor which depends on the shape of the crystal as well as the lattice structure, the two can be equated for suitably chosen shapes. A method for transforming these dipole sums into rapidly convergent sums of Bessel functions has been demonstrated. The rapid convergence of these sums assures the required shape independence of the Lorentz tensor components.

Computation of the Lorentz factors and their derivatives for othorhombic lattices has shown that

the internal fields are quite sensitive to lattice structure. Thus the assumption $L=\frac{1}{3}$ commonly used in dielectric theory can lead to large errors if the lattice is not cubic.

For lattices whose Lorentz tensors are diagonal, it is straightforward to include the effects of noncubic structure in the classical theory of macroscopic polarization in response to an applied field in the form of a modified Clausius-Mossotti relation, and to derive from this a structure-dependent "enhancement" factor for crystals containing polarizable molecules with a fixed permanent moment. For many crystal structures, this enhancement of P_0 turns out to be a reduction in consequence of negative Lorentz factors in one or two of the lattice directions.

Even for cubic crystals, changes of the Lorentz factors in response to small strains result in anisotropic response. Derivatives of the Lorentz factors have been shown to be as sensitive to crystal structure as are the Lorentz factors themselves, and should be accounted for in any theory involving changes in lattice dimensions.

ACKNOWLEDGMENT

The work of one of us (P.L.T.) was supported by the Army Research Office through Grant No. DAAG 29-78G-0064.

[1]J. H. P. Colpa, Physica 56, 185 (1971); 56, 205 (1971).
[2]E. C. Stoner, Philos. Mag. 36, 803 (1945).
[3]J. A. Osborn, Phys. Rev. 67, 351 (1945).
[4]M. B. E. Van der Hoff and G. C. Benson, Can. J. Phys. 31, 1087 (1953).
[5]S. Tripathy, A. J. Hopfinger, and P. L. Taylor, J. Phys. Chem. 85, 1371 (1981).
[6]M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1975), p. 255.
[7]I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals Series and Products* (Academic, New York, 1965), p. 340.
[8]Hans Mueller, Phys. Rev. 47, 947 (1935).