

## Effective Fields in Cubic Lattices with Extended Charges

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The effective field in cubic lattices is calculated for a simple model in which the electrons have spatially extended charge distributions. For simple cubic, body-centered cubic, and face-centered cubic lattices in which the electrons in each primitive cell are infinitesimally displaced from rigid cores, the effective field can be written  $\mathbf{E}_{\text{eff}} = \mathbf{E} + (4\pi/3)\gamma\mathbf{P}$ , where  $\mathbf{E}$  is the average electric field in the medium, and  $\mathbf{P}$  is the polarization. The coefficient  $\gamma$  varies from zero for very extended electronic charge distributions to 1 for the limit of point charges. Values of  $\gamma$  for Gaussian distributions of intermediate width are given. Effective fields are also calculated for the rocksalt, zincblende, and cesium chloride structures. These results involve an additional coefficient  $\gamma'$  which also varies between 0 and 1. For moderate overlaps between electronic charge distributions of next-nearest neighbors the effective fields differ appreciably from the Lorentz field  $\mathbf{E} + (4\pi/3)\mathbf{P}$ .

### I. INTRODUCTION

THE effective electric field<sup>1,2</sup> which acts on the atoms or ions or electrons in a crystal is of considerable importance in calculations of the optical properties of solids. We present here a simple classical calculation which shows how the magnitude of the effective field in several cubic lattices depends on the spatial extent of the electronic charge distribution on the atoms or ions.

We first consider cubic lattices with only one atom in the primitive cell, namely, the simple cubic (sc), body-centered cubic (bcc), and face-centered cubic (fcc) lattices, and assume that in each primitive cell the electrons are displaced a distance  $-\mathbf{d}$  with respect to the positive cores. If the core itself is rigid and unpolarized, the total polarization of the lattice is

$$\mathbf{P} = Nq\mathbf{d}, \quad (1)$$

where  $q$  is the magnitude of the charge of the electrons and of the cores in each cell, and  $N$  is the number of primitive cells per unit volume. For this simple model, the effective field can be written

$$\mathbf{E}_{\text{eff}} = \mathbf{E} + (4\pi/3)\gamma\mathbf{P}, \quad (2)$$

where  $\mathbf{E}$  is the macroscopic average electric field in the medium, and  $\gamma$  is an effective field constant whose value we shall calculate.

The two simple limiting cases of Eq. (2) are  $\gamma=0$  and  $\gamma=1$ . The first of these, for which the effective field is just the macroscopic field in the medium, leads to the Drude-Sellmeier formula

$$n^2 - 1 = 4\pi N\alpha \quad (3)$$

for the relation between the index of refraction  $n$  and the atomic polarizability  $\alpha$ . The case  $\gamma=1$ , which leads to the Lorentz field  $\mathbf{E}_{\text{eff}} = \mathbf{E} + (4\pi/3)\mathbf{P}$ , gives the Lorentz-Lorentz relation

$$(n^2 - 1)/(n^2 + 2) = (4\pi/3)N\alpha. \quad (4)$$

The most detailed investigation of effective fields is that of Darwin,<sup>3</sup> who showed that for free electrons in metals one has  $\gamma=0$ , while for self-contained atoms or ions one expects  $\gamma=1$ . Darwin's criteria suggest that one also has  $\gamma \sim 0$  for the electrons in the ionosphere.<sup>4</sup> Qualitatively one can understand the difference between the two cases by noting that a free electron has a uniform charge distribution, and therefore almost by definition feels the average field  $\mathbf{E}$  in the medium. On the other hand, a point charge feels only the local field, which will, in general, be different from the average field.

Mott and Gurney<sup>1</sup> long ago suggested that overlapping electronic charge distributions will lead to values of  $\gamma$  less than 1, but most calculations in nonmetallic solids use the Lorentz effective field. Many properties of solids, such as the lattice vibrations of ionic crystals<sup>5</sup> and the oscillator strengths of defects in ionic crystals,<sup>6</sup> depend for their quantitative interpretation on the magnitude of the effective field.

In this paper we give the results of a classical calculation of the effective field in cubic lattices based on the simplest possible model in which the spatial extent of the electron distribution can be readily considered. In the following section the effective field is calculated in some detail for the simple cubic, body-centered cubic, and face-centered cubic lattices; the resulting values of

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<sup>1</sup> N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1948), 2nd ed., Chap. I.

<sup>2</sup> W. K. H. Panofsky and M. Phillips, *Classical Electricity and Magnetism* (Addison-Wesley Publishing Company, Inc., Cambridge, Massachusetts, 1955), p. 31.

<sup>3</sup> C. G. Darwin, Proc. Roy. Soc. (London) **A146**, 17 (1934); **A182**, 152 (1943).

<sup>4</sup> J. A. Ratcliffe, *The Magneto-Ionic Theory and its Application to the Ionosphere* (Cambridge University Press, Cambridge, England, 1959), p. 154.

<sup>5</sup> M. Born and K. Huang, *The Dynamical Theory of Crystal Lattices* (Oxford University Press, London, 1954), Sec. 9.

<sup>6</sup> W. T. Doyle, Phys. Rev. **111**, 1072 (1958).

the effective field constant  $\gamma$  are presented in Sec. III. In Sec. IV we extend the model to cubic lattices with two atoms in the primitive cell, since most applications will be diatomic rather than to monatomic crystals.

## II. CALCULATION FOR MONATOMIC LATTICES

We shall assume that the atoms of the simple cubic, body-centered cubic, and face-centered cubic lattices which we consider contain some relatively loosely bound electrons, and some tightly bound electrons. The tightly bound electrons in real solids will contribute to the polarization and to the effective field, but for the sake of simplicity we ignore them here. We assume the loosely bound electrons to have a charge distribution  $-q\rho_e(\mathbf{r})$ , where  $\int \rho_e(\mathbf{r})d\mathbf{r}=1$ . In the numerical calculations we use a Gaussian charge distribution.

When an external electric field is applied, our model lattice will be polarized by a relative displacement  $\mathbf{d}$  between the cores and the electrons. We shall assume that this displacement is the same in every lattice cell; thus the polarization is given by Eq. (1). Our results apply only to lattice vibrations or electric fields of long wavelength.

The field acting on one of the atoms of the lattice is the external field plus the field of the other atoms. The field due to the atom itself is not included, since it is taken into account by the atomic polarizability  $\alpha$ . When the electrons have an extended charge distribution one must use some care in defining the effective field. We identify the effective field with the field that tends to separate the positive and negative charges in the atom. Thus the effective field is the field at the position of the core, or the integrated field acting on the electron distribution. We shall show formally below that these two are equal, as one would expect from the requirement that the total force on the charges in a primitive cell vanish.

The local field in the crystal can be written as the sum of four terms<sup>2,5</sup>:

$$\mathbf{E}_{\text{loc}} = \mathbf{E}_{\text{sph}} + \mathbf{E}_{\text{in}} + \mathbf{E}_{\text{out}} + \mathbf{E}_{\text{ext}}, \quad (5a)$$

where  $\mathbf{E}_{\text{sph}}$  is the field of the charges within an inscribed sphere,  $\mathbf{E}_{\text{in}}$  and  $\mathbf{E}_{\text{out}}$  are the fields arising from the charges on the inner and outer surfaces of the remainder of the sample, which is treated as a continuum with polarization  $\mathbf{P}$ , and  $\mathbf{E}_{\text{ext}}$  is the external field. The charges on the inner surface give  $\mathbf{E}_{\text{in}} = (4\pi/3)\mathbf{P}$ , and for samples of simple shapes the outer surface charges give a uniform field  $\mathbf{E}_{\text{out}} = -L\mathbf{P}$ , where  $L$  is the depolarization factor,<sup>7</sup> which is  $4\pi/3$  for a spherical sample and  $4\pi$  for a thin slab perpendicular to the external field. But the macroscopic field in the sample is

$$\mathbf{E} = \mathbf{E}_{\text{out}} + \mathbf{E}_{\text{ext}} = \mathbf{E}_{\text{ext}} - L\mathbf{P}, \quad (5b)$$

<sup>7</sup> C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1956), 2nd ed., p. 159.

so that we can write

$$\mathbf{E}_{\text{loc}} = \mathbf{E} + (4\pi/3)\mathbf{P} + \mathbf{E}_{\text{sph}}, \quad (5c)$$

which no longer depends on sample shape.

All that remains is the evaluation of  $\mathbf{E}_{\text{sph}}$ , the contribution of the atoms and ions in the inner sphere. If the lattice is composed of point dipoles and the center of the sphere is a point of cubic symmetry, then  $\mathbf{E}_{\text{sph}}$  vanishes there<sup>5</sup> and (5c) reduces to the Lorentz effective field. For our more general model, we want an expression for the field at any point in the primitive cell, since we must show that the average field acting on the electrons is the same as the field at the position of the cores. We sum first over all lattice points (or reciprocal lattice points) on a spherical shell, and then over shells, thus preserving the spherical summation required by (5c),<sup>8</sup> but we let the radius of the inner sphere become infinite. Our method of summation closely resembles the Ewald method for evaluating lattice sums.<sup>9</sup>

In a crystal the charge density  $\rho(\mathbf{r})$  and the electric field  $\mathbf{E}(\mathbf{r})$  have the lattice periodicity, and may be expanded in a Fourier series:

$$\rho(\mathbf{r}) = \sum_{\mathbf{k}_1} \rho_{\mathbf{k}_1} \exp(i\mathbf{k}_1 \cdot \mathbf{r}), \quad (6a)$$

$$\mathbf{E}(\mathbf{r}) = \sum_{\mathbf{k}_1} \mathbf{E}_{\mathbf{k}_1} \exp(i\mathbf{k}_1 \cdot \mathbf{r}). \quad (6b)$$

The summation is over the reciprocal lattice vectors  $\mathbf{k}_1$ , which have rectangular components  $2\pi l_1/a$ ,  $2\pi l_2/a$ , and  $2\pi l_3/a$ , respectively, where the  $l_i$  are integers and  $a$  is the lattice constant. For a simple cubic lattice the  $l_i$  take on all integral values. For a body-centered cubic space lattice the reciprocal lattice is face-centered, and  $l_1 + l_2 + l_3$  must be even. For a face-centered cubic space lattice, the  $l_i$  must be either all even or all odd.

If we neglect the magnetic fields associated with the lattice displacements,<sup>10</sup> Maxwell's equations  $\nabla \cdot \mathbf{E} = 4\pi\rho$  and  $\nabla \times \mathbf{E} = 0$  lead to

$$\mathbf{E}_{\mathbf{k}_1} = -4\pi i(\mathbf{k}_1/k_1^2)\rho_{\mathbf{k}_1}. \quad (6c)$$

The charge density in our model can be written

$$\rho(\mathbf{r}) = q \sum_{\mathbf{R}_i} \delta(\mathbf{r} - \mathbf{R}_i) - q \sum_{\mathbf{R}_i} \rho_e(\mathbf{r} - \mathbf{R}_i + \mathbf{d}), \quad (7)$$

where the Dirac delta functions of the cores are located at the lattice points  $\mathbf{R}_i$ , and the electronic charge distributions are displaced by  $-\mathbf{d}$ . The integration over the volume of the crystal required to obtain the coefficients in (6a) can be transformed to an integration over all space involving only the charge of the atoms or ions in one primitive cell.<sup>9</sup> We find

$$\rho_{\mathbf{k}_1} = (q/v)[1 - \sigma(\mathbf{k}_1) \exp(i\mathbf{k}_1 \cdot \mathbf{d})] = NqG(\mathbf{k}_1, \mathbf{d}), \quad (8a)$$

<sup>8</sup> The shape dependence of dipole sums is discussed by B. R. A. Nijboer and F. W. DeWette, *Physica* **14**, 422 (1958).

<sup>9</sup> See Appendix A of Ref. 7.

<sup>10</sup> See Sec. 8 of Ref. 5.

where  $v=N^{-1}$  is the volume of the primitive cell, and

$$\sigma(\mathbf{k}) = (2\pi)^{-3} \int \rho_e(\mathbf{r}) \exp(-i\mathbf{k}\cdot\mathbf{r}) d\mathbf{r} \quad (8b)$$

is the Fourier transform of the electronic charge distribution. From (6b) and (6c) we find

$$\mathbf{E}(\mathbf{r}) = \mathbf{E} - 4\pi i N q \sum_1' (\mathbf{k}_1/k_1^3) G(\mathbf{k}_1, \mathbf{d}) \exp(i\mathbf{k}_1\cdot\mathbf{r}), \quad (9)$$

where the prime on the summation indicates that the term with  $\mathbf{k}_1=0$  has been omitted. This term is just  $\mathbf{E}$ , the average electric field in the medium, and is written in explicitly.

The field acting on the atom at the origin due to the external field and all the other atoms in the crystal is obtained by subtracting from (9) the field due to the atom's own charge. We find

$$\rho_{\text{self}}(\mathbf{r}) = (2\pi)^{-3} q \int G(\mathbf{k}, \mathbf{d}) \exp(i\mathbf{k}\cdot\mathbf{r}) d\mathbf{k}, \quad (10a)$$

$$\mathbf{E}_{\text{self}}(\mathbf{r}) = -(2\pi^2)^{-1} i q \int (\mathbf{k}/k^2) G(\mathbf{k}, \mathbf{d}) \exp(i\mathbf{k}\cdot\mathbf{r}) d\mathbf{k}, \quad (10b)$$

where the integration is over all values of  $\mathbf{k}$ . We subtract (10b) from (9) and find the local field due to all atoms except the one in the central cell to be

$$\begin{aligned} \mathbf{E}_{\text{loc}}(\mathbf{r}) = & \mathbf{E} + (2\pi^2)^{-1} i q \int [1 - 8\pi^3 N \sum_1' \delta(\mathbf{k} - \mathbf{k}_1)] \\ & \times (\mathbf{k}/k^2) G(\mathbf{k}, \mathbf{d}) \exp(i\mathbf{k}\cdot\mathbf{r}) d\mathbf{k}. \quad (11) \end{aligned}$$

We can now verify that the local field acting on the core at the origin is equal to the average field acting on the electrons from that atom. These two fields are given, respectively, by

$$\begin{aligned} \mathbf{E}_{\text{loc}}(0) = & \mathbf{E} + -(2\pi^2)^{-1} i q \int [1 - 8\pi^3 N \sum_1' \delta(\mathbf{k} - \mathbf{k}_1)] \\ & \times (\mathbf{k}/k^2) \sigma(\mathbf{k}) \exp(i\mathbf{k}\cdot\mathbf{d}) d\mathbf{k}, \quad (12a) \end{aligned}$$

$$\begin{aligned} & \int \mathbf{E}_{\text{loc}}(\mathbf{r}) \rho_e(\mathbf{r} + \mathbf{d}) d\mathbf{r} \\ & = \mathbf{E} + (2\pi^2)^{-1} i q \int [1 - 8\pi^3 N \sum_1' \delta(\mathbf{k} - \mathbf{k}_1)] \\ & \quad \times (\mathbf{k}/k^2) \sigma(-\mathbf{k}) \exp[-i\mathbf{k}\cdot\mathbf{d}] d\mathbf{k}, \quad (12b) \end{aligned}$$

where certain terms which vanish because of the odd parity of the integral have been omitted. If we substitute  $-\mathbf{k}$  for  $\mathbf{k}$  in (12b), it becomes identical to (12a), and the two effective fields are equal.

Since we are interested only in effects linear in the polarization, we retain only the terms linear in  $\mathbf{d}$ , and

find that the effective field is

$$\begin{aligned} \mathbf{E}_{\text{eff}} = & \mathbf{E} + (2\pi^2)^{-1} v \int \mathbf{k}(\mathbf{k}\cdot\mathbf{P}) k^{-2} \sigma(\mathbf{k}) d\mathbf{k} \\ & - 4\pi \sum_1' \mathbf{k}_1(\mathbf{k}_1\cdot\mathbf{P}) k_1^{-2} \sigma(\mathbf{k}_1), \quad (13a) \end{aligned}$$

where Eq. (1) was used to eliminate  $\mathbf{d}$ . If we restrict ourselves to spherically symmetric  $\rho_e(\mathbf{r})$  and  $\sigma(\mathbf{k})$ , the cubic symmetry of the cases we consider allows us to replace  $\mathbf{k}_1(\mathbf{k}_1\cdot\mathbf{P}) k_1^{-2}$  by  $\frac{1}{3}\mathbf{P}$  in the summation, and a similar simplification occurs in the integral in (13). Thus the effective field is

$$\mathbf{E}_{\text{eff}} = \mathbf{E} + (4\pi/3) \mathbf{P} [v\rho_e(0) - \sum_1' \sigma(\mathbf{k}_1)] \quad (13b)$$

and the effective field coefficient  $\gamma$  of Eq. (2) is

$$\gamma = v\rho_e(0) - \sum_1' \sigma(\mathbf{k}_1). \quad (13c)$$

We can convert (13c) to a summation in the direct lattice if we replace  $\sigma(\mathbf{k}_1)$  by its definition in (8b) and interchange the order of integration and summation. We find

$$\gamma = 1 - v \sum_{\mathbf{R}_i} \rho_e(\mathbf{R}_i). \quad (14)$$

To proceed with the explicit evaluation of  $\gamma$  we now assume that the electronic charge distribution is a Gaussian.

$$\rho_e(\mathbf{r}) = (w/\pi)^{3/2} \exp(-w\mathbf{r}^2). \quad (15)$$

If we introduce the dimensionless constant  $B = wa^2$ , Eq. (13c) gives

$$\gamma = (B/\pi)^{3/2} (v/a^3) - \sum_1' \exp(-\pi^2 l^2/B), \quad (16)$$

where  $l^2 = l_1^2 + l_2^2 + l_3^2$ , and the  $l_i$  take on the values already discussed for the three cubic lattices. The primitive cell volume  $v$  equals  $a^3$ ,  $\frac{1}{2}a^3$ , and  $\frac{1}{4}a^3$  for the simple cubic, body-centered cubic, and face-centered cubic lattices, respectively.

The reciprocal lattice sums in (16) are conveniently expressed in terms of the sums

$$S_+(B) = \sum_{m=-\infty}^{\infty} \exp(-\pi^2 m^2/B), \quad (17a)$$

$$\begin{aligned} S_-(B) = & \sum_{m=-\infty}^{\infty} (-1)^m \exp(-\pi^2 m^2/B) \\ & = 2S_+(B/4) - S_+(B). \quad (17b) \end{aligned}$$

The convergence of these sums is very rapid when  $B$  is small, but becomes slow for large  $B$ . Then we can use the theta function transformation<sup>11</sup>

$$\begin{aligned} & \sum_{m=-\infty}^{\infty} \exp[-(m\pi - z)^2/B] = (B/\pi)^{1/2} \\ & \quad \times \sum_{m=-\infty}^{\infty} \exp(-Bm^2 + 2imz). \quad (18) \end{aligned}$$

<sup>11</sup> E. T. Whittaker and G. N. Watson, *A Course of Modern Analysis* (Cambridge University Press, Cambridge, England, 1927), 4th ed., p. 476.

TABLE I. Effective field constants and fractional charges for cubic lattices. The effective field constants  $\gamma$  and  $\gamma'$  are given in Eqs. (20) and (29), respectively, and  $f$  is the fraction of the electronic charge on one atom which is contained within the atomic polyhedron centered at that atom.  $B$  is the width parameter  $wa^2$  for the electron distribution, where  $w$  is given in Eq. (15) and  $a$  is the lattice constant.

$B$	Simple cubic		Body-centered cubic		Face-centered cubic		Rocksalt	Zincblende	Cesium chloride
	$f$	$\gamma$	$f$	$\gamma$	$f$	$\gamma$	$\gamma'$	$\gamma'$	$\gamma'$
0.25	0.0211	0.002448	0.0108	0.011224	0.0055	0.005612	0.000000	0.000000	0.000000
0.5	0.0561	0.063494	0.0295	0.031747	0.0151	0.015873	0.000000	0.000000	0.000000
0.75	0.0972	0.116634	0.0522	0.058323	0.0272	0.029161	0.000000	0.000000	0.000012
1.0	0.1410	0.179277	0.0776	0.089794	0.0409	0.044897	0.000000	0.000000	0.000310
1.5	0.2309	0.321570	0.1327	0.164938	0.0718	0.082481	0.000000	0.000000	0.008306
2.0	0.3182	0.464174	0.1905	0.253354	0.1057	0.126984	0.000003	0.000000	0.042534
2.5	0.3994	0.589576	0.2485	0.350471	0.1412	0.177412	0.000057	0.000001	0.111366
3.0	0.4733	0.692524	0.3052	0.449911	0.1776	0.232865	0.000402	0.000012	0.207298
3.5	0.5396	0.773809	0.3598	0.545238	0.2142	0.292209	0.001619	0.000076	0.316668
4.0	0.5984	0.836261	0.4117	0.631727	0.2506	0.353985	0.004569	0.000310	0.427192
5	0.6959	0.917728	0.5064	0.769959	0.3216	0.478282	0.019208	0.002232	0.622189
6	0.7704	0.960551	0.5886	0.862990	0.3889	0.593957	0.049183	0.008306	0.765429
7	0.8270	0.981769	0.6588	0.921072	0.4517	0.693583	0.094969	0.021171	0.860374
8	0.8696	0.991816	0.7181	0.955617	0.5096	0.774522	0.153826	0.042534	0.919419
9	0.9017	0.996409	0.7678	0.975495	0.5625	0.837465	0.221669	0.072823	0.954581
10	0.9259	0.998453	0.8091	0.986663	0.6106	0.884808	0.294345	0.111366	0.974872
12	0.9577	0.999725	0.8717	0.996177	0.6930	0.944417	0.440631	0.207298	0.992630
14	0.9757	0.999954	0.9141	0.998941	0.7593	0.974253	0.573365	0.316668	0.997928
16	0.9860	0.999992	0.9427	0.999714	0.8121	0.988431	0.684090	0.427192	0.999435
20	0.9953	1.000000	0.9746	0.999980	0.8864	0.997812	0.837645	0.622189	0.999961
25	0.9988	1.000000	0.9908	0.999999	0.9401	0.999749	0.934996	0.793255	0.999999
30	0.9997	1.000000	0.9967	1.000000	0.9686	0.999973	0.975519	0.893573	1.000000
35	0.9999	1.000000	0.9988	1.000000	0.9836	0.999997	0.991161	0.947481	1.000000
40	1.0000	1.000000	0.9996	1.000000	0.9915	1.000000	0.996907	0.974872	1.000000
50	1.0000	1.000000	0.9999	1.000000	0.9977	1.000000	0.999645	0.994615	1.000000

If  $z=0$  this gives

$$S_+(B) = (B/\pi)^{1/2} S_+(\pi^2/B). \quad (19)$$

Thus even for the worst case ( $B=\pi$ ) no more than three terms in  $m^2$  need to be used to give a relative error of  $\exp(-9\pi)$  or less. Use of Eq. (18) is equivalent to using Eq. (14) instead of Eq. (13c) to calculate  $\gamma$ .

For the simple cubic lattice, Eq. (16) gives

$$\gamma_{sc} = 1 + (B/\pi)^{3/2} - S_+^3(B), \quad (20a)$$

where the 1 arises from the point  $\mathbf{l}=0$  that is excluded from the sum in (16). For the body-centered cubic space lattice we omit points for which  $l_1+l_2+l_3$  is odd, and obtain

$$\gamma_{bcc} = 1 + \frac{1}{2}(B/\pi)^{3/2} - \frac{1}{2}[S_+^3(B) + S_-^3(B)]. \quad (20b)$$

For the face-centered cubic space lattice, we must include only  $l_i$  which are all even or all odd, and find:

$$\gamma_{fcc} = 1 + \frac{1}{4}(B/\pi)^{3/2} - \frac{1}{8}[S_+(B) + S_-(B)]^3 - \frac{1}{8}[S_+(B) - S_-(B)]^3. \quad (20c)$$

### III. RESULTS FOR MONATOMIC LATTICES

The numerical values of  $\gamma$  for the simple cubic, body-centered cubic, and face-centered cubic lattices given in (20) have been evaluated for a series of values of the

width parameter  $B$ , and are listed in Table I. We see that they vary smoothly between the expected limits,  $\gamma=0$  for the extreme diffuse limit  $B=0$ , and  $\gamma=1$  for electronic point charges,  $B \rightarrow \infty$ .

It is instructive to present the results not in terms of  $B$  but in terms of a parameter that measures the compactness of the electronic charge more directly. We use for this purpose the quantity

$$f = \int_{\text{cell}} \rho_e(\mathbf{r}) d\mathbf{r}, \quad (21)$$

which is the fraction of the electronic charge contained in the atomic polyhedron<sup>12</sup> centered at the center of the charge distribution. Values of  $f$  obtained by numerical integration are given for each value of  $B$  in Table I for the three structures. For the simple cubic case we can check the numerical integration, since (21) then gives

$$f_{sc}(B) = [\text{erf}(\frac{1}{2}B^{1/2})]^3. \quad (22)$$

The listed values which were checked were correct to the four decimal places given, and we expect the error in the remaining values, and for the other structures, to be no more than one or two units in the last place given. The numerical integration converges most slowly for

<sup>12</sup> See p. 286 of Ref. 7.

the fcc lattice, probably because of the rather sharp corners in the primitive cell. The evaluation of  $\gamma$  is numerically much simpler, and the values are given to six decimals.

The effective field coefficients  $\gamma$  for the simple cubic and face-centered cubic lattices are shown as functions of  $f$  in Fig. 1. The curve for the body-centered cubic lattice falls very close to the fcc curve, and has therefore been omitted.

For diffuse electronic charge distributions we find that  $\gamma \sim f$  for very small values of  $f$ . When the overlap between neighboring electron distributions, as measured by  $1-f$ , goes to zero, we find that for the Gaussian case  $1-\gamma \sim (1-f)^p$ , where  $p$  goes asymptotically to 4 as the overlap goes to zero. This dependence is specific to the Gaussian distribution. If, as is perhaps more reasonable for real solids, we have charge densities which decay exponentially at large distances, then  $p$  approaches 2 in the limit of small overlap.

The most striking qualitative feature of the results in Fig. 1 is that even for an overlap of 20%, i.e.,  $f=0.8$ ,  $\gamma$  differs from 1 by less than 3%. This conclusion will be weakened somewhat if charge distributions with an exponential tail are considered instead of the Gaussian distribution we chose for its simplicity, but it suggests that for the monatomic cubic lattices the Lorentz field is quite accurate until there is very substantial electronic overlap.

#### IV. DIATOMIC LATTICES

Most calculations involving effective fields in real solids are carried out for diatomic structures, which include many of the ionic crystals and semiconductors for which relevant experiments have been carried out. We therefore extend our results to the rocksalt, zincblende, and cesium chloride structures, each of which has two atoms (or ions) in the primitive cell.

We assume that the negative ions in the undisturbed lattice are at the lattice points, and that the positive ions are displaced by a basis vector  $\mathbf{b}$ . The rectangular components of  $\mathbf{b}$  are  $\frac{1}{2}a, 0, 0$ ;  $\frac{1}{4}a, \frac{1}{4}a, \frac{1}{4}a$ ; and  $\frac{1}{2}a, \frac{1}{2}a, \frac{1}{2}a$ ; for the rocksalt, zincblende, and cesium chloride structures, respectively, where  $a$  is the lattice constant. The first two of these lattices have a face-centered cubic Bravais lattice, while the last has a simple cubic Bravais lattice.

The charges of the loosely bound electrons associated with the positive and negative ions, are  $q_{+e}$  and  $q_{-e}$ , respectively, and the displacements of the electrons from their equilibrium positions are  $\mathbf{u}_{+e}$  and  $\mathbf{u}_{-e}$ , respectively. Similarly we assume that the rigid cores of the positive and negative ions have charges and displacements  $q_{+c}$ ,  $\mathbf{u}_{+c}$  and  $q_{-c}$ ,  $\mathbf{u}_{-c}$ , respectively. The total polarization of the lattice is

$$\mathbf{P} = N(q_{+c}\mathbf{u}_{+c} + q_{+e}\mathbf{u}_{+e} + q_{-c}\mathbf{u}_{-c} + q_{-e}\mathbf{u}_{-e}), \quad (23)$$

and charge neutrality requires that

$$q_{+c} + q_{+e} + q_{-c} + q_{-e} = 0. \quad (24)$$

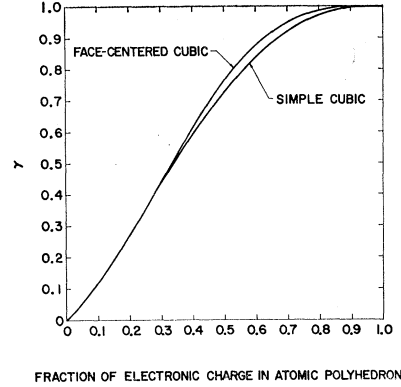


FIG. 1. The effective field constant  $\gamma$ , as given in Eq. (20) for the simple cubic and face-centered cubic lattices, is plotted versus  $f$ , the fraction of the electronic charge of one atom which lies within the atomic polyhedron centered at the atom. The curve for the body-centered cubic lattice would practically coincide with the fcc curve.

The calculation of the effective field acting on the cores and the electrons of the two ions proceeds exactly as in Sec. II, and will not be described. For each of the two ions, we subtract the field of the ion itself from the total field in the lattice to get the effective field acting on the core and electrons of that ion. We find the effective fields to be

$$\mathbf{E}_{+c} = \mathbf{E} + (4\pi N/3)[\gamma_{+q_{+e}}(\mathbf{u}_{+e} - \mathbf{u}_{+c}) + q_{-c}(\mathbf{u}_{-c} - \mathbf{u}_{+c}) + \gamma'_{-q_{-e}}(\mathbf{u}_{-e} - \mathbf{u}_{+c})], \quad (25a)$$

$$\mathbf{E}_{+e} = \mathbf{E} + (4\pi N/3)[\gamma_{+q_{+c}}(\mathbf{u}_{+c} - \mathbf{u}_{+e}) + \gamma'_{+q_{-c}}(\mathbf{u}_{-c} - \mathbf{u}_{+e}) + \gamma'_{r'q_{-e}}(\mathbf{u}_{-e} - \mathbf{u}_{+e})], \quad (25b)$$

$$\mathbf{E}_{-c} = \mathbf{E} + (4\pi N/3)[q_{+c}(\mathbf{u}_{+c} - \mathbf{u}_{-c}) + \gamma'_{+q_{+e}}(\mathbf{u}_{+e} - \mathbf{u}_{-c}) + \gamma_{-q_{-e}}(\mathbf{u}_{-e} - \mathbf{u}_{-c})], \quad (25c)$$

$$\mathbf{E}_{-e} = \mathbf{E} + (4\pi N/3)[\gamma'_{-q_{+c}}(\mathbf{u}_{+c} - \mathbf{u}_{-e}) + \gamma'_{r'q_{+e}}(\mathbf{u}_{+e} - \mathbf{u}_{-e}) + \gamma_{-q_{-c}}(\mathbf{u}_{-c} - \mathbf{u}_{-e})], \quad (25d)$$

where, for example,  $\mathbf{E}_{-e}$  is the effective field acting on the electrons of the negative ion. Here  $\gamma$  is the effective field constant for the Bravais lattice (fcc for rocksalt and zincblende, sc for cesium chloride) as given in Eq. (20), and the subscript  $+$  or  $-$  indicates that we must use for the parameter  $B = wa^2$  the value  $B_+$  or  $B_-$  appropriate for the electron distributions on the positive or negative ions, respectively. The new coefficient  $\gamma'$  is defined by

$$\gamma' = 1 - \sum_1 \sigma(\mathbf{k}_1) \exp(i\mathbf{k}_1 \cdot \mathbf{b}), \quad (26)$$

where the sum is over all reciprocal lattice vectors, and  $\mathbf{b}$  is the basis vector for the particular lattice. For the Gaussian<sup>13</sup> charge distribution of Eq. (15), this gives

$$\gamma' = 1 - \sum_1 \exp[(-\pi^2 l^2 / B) + (2\pi/a)\mathbf{l} \cdot \mathbf{b}], \quad (27)$$

where  $\mathbf{l}$  has the same significance as in Sec. II. The

<sup>13</sup> A Gaussian model was used to calculate crystal potentials by J. L. Birman, Phys. Rev. **97**, 897 (1955).

subscripts + and - on  $\gamma'$  have the same significance as for  $\gamma$ , and the subscript  $r$  means that we must use for  $B$  the value  $B_r = B_+ B_- / (B_+ + B_-)$ .

The effective field expressions in (26) have the expected values in some simple limiting cases. For example, if  $B_+$  and  $B_-$  (and therefore, also  $B_r$ ) become infinite, corresponding to compact electron distributions, both  $\gamma$  and  $\gamma'$  go to 1, and we can verify that all four effective fields reduce to the Lorentz field by using Eqs. (23) and (24). If one of the electron distributions becomes very broad, corresponding to  $B \sim 0$ , the associated values of  $\gamma$  and  $\gamma'$ , including  $\gamma_r$ , go to zero, and the effective field acting on that electron becomes just the average electric field  $\mathbf{E}$ . The effective field acting on the cores does not, and should not, go to  $\mathbf{E}$  in this case. One further check on the expressions in (25) is that the total force on the four charges in the primitive cell vanishes identically.

When we substitute in Eq. (26) the values of  $\mathbf{b}$  appropriate for the rocksalt, zincblende, and cesium chloride lattices, we find that in each case  $\gamma'$  can be written

$$\gamma' = 1 - \sum_a \exp(-\pi^2 l_a^2 / B) + \sum_b \exp(-\pi^2 l_b^2 / B). \quad (28)$$

For the rocksalt structure the first summation is over values of the  $l_i$  all of which are even, and the second summation is over values which are all odd. Thus, in the notation of the previous section

$$\gamma'(B) = 1 - \frac{1}{8} [S_+(B) + S_-(B)]^3 + \frac{1}{8} [S_+(B) - S_-(B)]^3 \quad (\text{rocksalt}). \quad (29a)$$

For the zincblende lattice, the first sum in (26) is over values of the  $l_i$  which are all even and whose sum is divisible by 4, and the second sum is over the remaining even values. For this case we find

$$\gamma'(B) = 1 - [S_-(B/4)]^3 \quad (\text{zincblende}). \quad (29b)$$

Finally for the cesium chloride lattice the first sum in (26) is over  $l_i$  whose sum is even, and the second sum is over  $l_i$  whose sum is odd, and we have

$$\gamma'(B) = 1 - [S_-(B)]^3 \quad (\text{cesium chloride}). \quad (29c)$$

Values of  $\gamma'$  for the three diatomic cubic lattices are given for various values of  $B$  in Table I. If we characterize the electron distribution by the quantity  $f$  for the Bravais lattice ( $f$  describes the overlap of the electrons with others of the same sublattice), we can plot  $\gamma'$  against  $f$ . These curves are shown in Fig. 2.

The rapid decrease in  $\gamma'$  when  $f$  decreases from 1 arises because  $\gamma'$  depends on nearest-neighbor overlap, while  $f$  measures the overlap between next-nearest neighbors. We see from Fig. 2 that even a small overlap between next-nearest-neighbor charge distributions implies a marked departure of  $\gamma'$  from 1, and therefore a marked departure of the effective field from the Lorentz field.

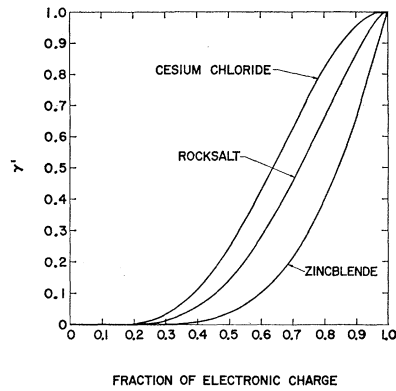


Fig. 2. The effective field constant  $\gamma'$  for the rocksalt, zincblende, and cesium chloride structures, given in Eq. (29), is plotted versus the charge fraction  $f$  in the atomic polyhedron for the corresponding Bravais lattice.

The asymptotic dependence of  $\gamma$  on  $f$  is given by  $1 - \gamma \sim (1 - f)^p$ , where for Gaussian charge distributions  $p$  approaches 2,  $\frac{3}{2}$ , and 3, respectively, for the rocksalt, zincblende, and cesium chloride lattices as  $f \rightarrow 1$ . If the charge distribution has an exponential tail, these values of  $p$  must be replaced by their square roots.

The polarization of the tightly bound electrons, which has been neglected in our treatment so far, can be taken into account by a straightforward extension of Eq. (25). We will have an additional effective field expression for each group of tightly bound electrons, and their displacements will enter in the effective fields acting on the remaining charges in the lattice. It is not possible to simplify all the resulting expressions in such a way that only the net polarization of the tightly bound electrons appears.

## V. DISCUSSION

The results of the previous section show that the effective fields can deviate substantially from the Lorentz field when there is overlap of the electron distributions. This was pointed out by Mott and Gurney,<sup>1</sup> and has recently been considered by Brodsky and Burstein<sup>14</sup> in relation to the effective charge in III-V semiconductors. Our results may be helpful in making possible crude quantitative estimates of the effective field for actual crystals.

In applying our results to the oscillator strengths of defects in ionic crystals, one must take into account the corrections which results because the defect has different properties from those of the defect site in a perfect crystal. These corrections have been discussed by Herring.<sup>15</sup>

For application to the theory of lattice vibrations we

<sup>14</sup> M. H. Brodsky and E. Burstein, *Bull. Am. Phys. Soc.* **7**, 214 (1962).

<sup>15</sup> C. Herring, in *Photoconductivity Conference*, edited by R. G. Breckenridge, B. R. Russell, and E. E. Hahn (John Wiley & Sons, Inc., New York, 1956), p. 81.

note that the effective fields in (25) depend only on differences of displacements, and therefore lead to force terms of the same form as the short-range "elastic" interactions. Thus the equations of motion of the lattice<sup>16</sup> will be unchanged, and the only effect of the corrections we have found to the Lorentz effective field will be to change the interpretation of some of the coefficients in the equations of motion for the long-wavelength optical modes.

Effective fields for waves of arbitrary wavelength have recently been considered by Cochran.<sup>17</sup> His results

<sup>16</sup> See, for example, Eq. (3.2) of W. Cochran, in *Advances in Physics*, edited by B. H. Flowers (Taylor and Francis, Ltd. London, 1960), Vol. 9, p. 387.

<sup>17</sup> W. Cochran, Proc. Roy. Soc. (London) **A276**, 308 (1963);

are for rigid ions but, if modified to allow for separate displacements of the core and one or more electron shells, they are equivalent in the long-wavelength limit to the results given here.

#### ACKNOWLEDGMENTS

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Proceedings of the International Conference on Lattice Dynamics, Copenhagen, 1963 (to be published). We are indebted to Dr. Cochran for sending us his results prior to publication.

## Spin-Wave Renormalization Applied to Ferromagnetic CrBr<sub>3</sub>†

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Nuclear-magnetic-resonance-domain magnetization data for ferromagnetic CrBr<sub>3</sub> have been extended over the range 1–20°K. Using the low-temperature ( $\leq 5.25^\circ\text{K}$ ) data and Holstein-Primakoff spin-wave theory without the usual long-wavelength approximation, we have shown that exchange constants reported by Gossard, Jaccarino, and Remeika are in error by about 40%. This error resulted from the long-wavelength approximation, which causes, even at temperatures  $\frac{1}{4}$ th the Curie temperature, errors much larger than experimental errors. In the low-temperature range, we have found a 20% range for the values of the exchange constants which will explain the experimental results. However, by using spin-wave renormalization techniques to interpret the intermediate temperature data, the acceptable range in values for the exchange constants is narrowed to less than 2%. We have been able to fit the experimental NMR frequencies, throughout the temperature range of 1–20°K, with the renormalized spin-wave theory. The resulting rms error of 16.2 kc/sec lies within the mean experimental error, thereby giving experimental verification to the approximations used in developing the spin-wave renormalization. This data fit gives 8.25°K for the intralayer exchange constant, 0.497°K for the interlayer exchange constant, and 58.099 Mc/sec for the 0°K, zero-field Cr<sup>53</sup> resonance frequency.

### I. INTRODUCTION

CONSIDERABLE interest has been shown in recent years in comparisons of experimental results with predictions of the Heisenberg model of magnetism; e.g., measurements of the magnetization of a variety of magnetically ordered crystals have been made and the results interpreted by spin-wave theories of varying degrees of sophistication.<sup>1</sup> In particular, two nuclear-magnetic-resonance (NMR) magnetization measurements and their interpretations have a bearing on the present investigation: (1) The work of Gossard, Jaccarino, and Remeika<sup>2</sup> (hereafter referred to as GJR) on

ferromagnetic CrBr<sub>3</sub>, and (2) the work of Narath<sup>3</sup> on antiferromagnetic CrCl<sub>3</sub>. At low temperatures, the structures of these crystals are isomorphic,<sup>4</sup> and can be represented by Fig. 1 (a). In both cases, the strongest exchange coupling is the ferromagnetic coupling  $J_T$ , of nearest neighbors in the hexagonal basal plane. The interlayer exchange coupling  $J_L$  is ferromagnetic in CrBr<sub>3</sub> and antiferromagnetic in CrCl<sub>3</sub>.

We have noticed an inconsistency between  $J_T$  reported for CrBr<sub>3</sub> and the one reported for CrCl<sub>3</sub>; that is, for CrCl<sub>3</sub> the value  $J_T/k = 4.5^\circ\text{K}$  obtained via spin-wave theory is considerably larger than the one deduced from the ordering temperature  $T_c$  by means of the molecular field approximation

$$J_T/k = 3T_c/[2zS(S+1)], \quad (1.1)$$

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<sup>1</sup> Exhaustive references may be found in the review article of P. W. Anderson, *Solid State Phys.* **14**, 99 (1963).

<sup>2</sup> A. C. Gossard, V. Jaccarino, and J. P. Remeika, *Phys. Rev. Letters* **7**, 122 (1961).

<sup>3</sup> A. Narath, *Phys. Rev. Letters* **7**, 410 (1961); *Phys. Rev.* **131**, 1929 (1963).

<sup>4</sup> B. Morosin and A. Narath, *J. Chem. Phys.* **40**, 1958 (1964).