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# A classical electrostatic model for tetragonal single crystals of barium titanate

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## Contents

Experimental observations of the ionic coordinates in single crystals of tetragonal barium titanate, together with theoretical estimates of the ionic charges, are taken

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as the starting point of a classical analysis of an electrostatic model of the crystal in which each ion is represented by a point charge carrying a point dipole; this dipole represents that arising from the electronic polarizability of the ion of the crystal. The positions occupied by the ions are such that their charges cause ionic polarization of the unit cells of the crystal. The charges also cause an electric field to exist at each ion; its calculation is based upon the Lorentz formula for internal field, but with a crucial difference in the manner of its application from the manner in which it previously has been applied. The ion exhibits electronic polarization caused not only by the field acting on it due to ionic charges, but also by that due to the electronic dipoles created at all other ions; the electronic polarization process is consequently highly interactive. These considerations lead to the derivation of an equation which must be satisfied if the spontaneous polarization is to be predicted; a similar procedure leads to another independent equation for the prediction of the refractive index. The electronic polarizabilities of the ions are constituents of each of these equations, and the insertion into them of literature values for the electronic polarizabilities of the barium and titanium ions permits the evaluation of the electronic polarizabilities of the oxygen ions in their two different crystallographic positions. The fields acting at, and the electrostatic forces acting on, each ion are then calculated.

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## 1. Introduction

Barium titanate, one of the perovskite ferroelectrics, can exist in several crystallographic forms. Above a transition temperature of about 120 °C it is cubic, although for the very pure material, a temperature of 130 °C has been proposed (Johnson 1965). There is a barium ion at each corner, an oxygen ion in the centre of each face, and a titanium ion in the centre of each unit cube (figure 1$a$), so that the chemical formula of the material is $BaTiO_3$. On cooling through the transition temperature the material becomes ferroelectric; those edges of the cube conventionally designated as being in the $x$ and $y$ directions slightly contract by an equal amount, while those conventionally designated as being in the $z$ direction elongate so that they are about 1% longer than the other edges. The structure has thus become tetragonal and remains so until the next transition temperature of about 5 °C is reached, below which the structure becomes orthorhombic. This paper is entirely concerned with the behaviour of single crystals of the material in its tetragonal form.

In the absence of an applied field, considerations of symmetry show that the cubic crystal would not exhibit any polarization. The change from cubic to tetragonal structure is accompanied by some displacement of the ions relative to each other (figure 1$b$). With regard to the barium ions, the titanium ions (positive) are displaced in the $+z$ direction, while the oxygen ions (negative) are displaced in the $-z$ direction. In the tetragonal form the crystal therefore exhibits a polarization in the $+z$ direction. Since this exists without the presence of an externally applied electric field, it is termed a spontaneous polarization; its reported experimental values for single crystals are in reasonable agreement (Merz 1953; Wemple *et al.* 1968). The value adopted for this analysis will be the same as that adopted by Sommer *et al.* (1990), namely $0.261\ C\ m^{-2}$ (SI units will be used throughout this paper).

The model used will only take account of ionic displacements in the $z$ direction. Although other possibilities have been discussed from time to time, such as the time-
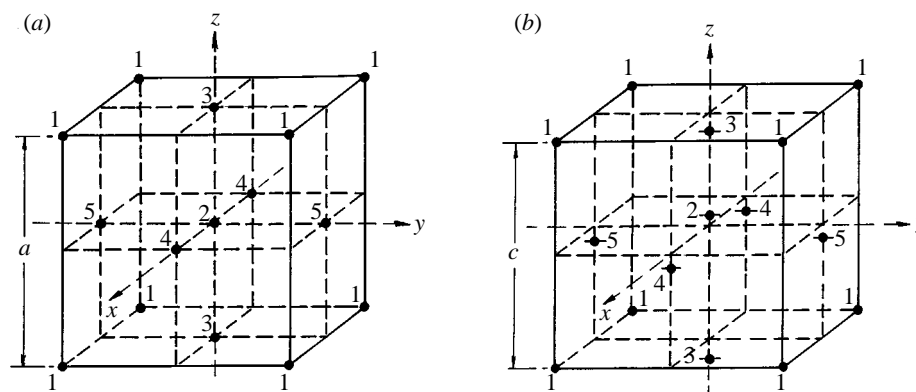
Figure 1. The unit cell of the barium titanate crystal. The ions Ba, Ti, $O_a$, $O_{b(i)}$, $O_{b(ii)}$ are represented by the figures 1, 2, 3, 4, 5 respectively. The cubic form is shown in $(a)$, where $a = 3.992 \times 10^{-10}$ m. The tetragonal form is shown in $(b)$, where $c = 1.01a$; the ionic displacements are given in table 1.

dependent displacements of an ion in each of the four [111] directions, so that its displacement in the $z$ direction becomes a resolved component of its time-dependent displacement, such refinements will not be introduced into the analysis. The objective is to find out what can be predicted by the use of a simple classical static model, each ion being considered as a point charge carrying a point dipole, representing the real ion of the crystal which has a charge and also has a dipole resulting from the displacement of its electron cloud relative to its nucleus. The electronic polarizabilities of the ions will be taken to be constants, independent of the field acting on them. This model is similar to that adopted by Hagedorn (1952), but his treatment did not give a satisfactory prediction of the magnitude of the spontaneous polarization.

Although the treatment to follow relates to the tetragonal structure, the expression derived by Lorentz (1952) for the field created by an infinite array of point dipoles which form a cubic lattice will be used (the reference is to a reprint of the book originally published in 1909). This will introduce some error, but in view of other uncertainties involved in the calculation, it was felt that, following earlier practice, for the purpose of the application of the Lorentz expression to the $BaTiO_3$ tetragonal structure, it could reasonably be regarded as a small deformation of the cubic phase.

The nominal charge on each barium, titanium, and oxygen ion is $+2e$, $+4e$ and $-2e$ respectively, where $e$ is the magnitude of the charge on the electron. However, theoretical studies by Cohen & Krakauer (1990) have shown that while the figure of $+2e$ for the barium ion is likely to be about right, there is in effect a considerable donation of electrons to the titanium ion from each oxygen ion, so that their charges are about $+2.89e$ and $-1.63e$ respectively. These are the values for the ionic charges adopted for this paper.

Referring to the cubic form shown in figure 1$a$, and taking the titanium ion as the origin of conventional Cartesian axes, oxygen ions lying on the $x$, $y$, and $z$ axes are designated $O_{b(i)}$, $O_{b(ii)}$ and $O_a$ respectively. Although they are in crystallographically identical positions in the cubic phase, in the tetragonal phase brought about by ionic movement in the $z$ direction, the $O_a$ ion is in a different crystallographic position from that of the other two. The crystallographic positions of the latter still remain indistinguishable from each other, but for the purpose of analysis it is expedient to keep a distinction between them by retaining the designations $O_{b(i)}$ and $O_{b(ii)}$. For

convenience, the subscript $k$ will be used, having values of 1, 2, 3, 4, 5 to indicate that quantities relate to the Ba, Ti, $O_a$, $O_{b(i)}$, $O_{b(ii)}$ ions respectively. Where the quantities are consequent on the actions of other ions, the subscript $j$ will be used to indicate the causative ion; again, $j$ runs from 1 to 5.

The analysis which follows makes use of the Lorentz formula for the internal field at the lattice points, modified where necessary to give the field at other principal points in the unit cell. Attempts to analyse the behaviour of single crystals of barium titanate in the tetragonal phase which make use of these formulae have appeared sporadically since about 1950, but as has been pointed out by Sommer *et al.* (1990), experimental values of spontaneous polarization and refractive index so far have not been predicted. As they remark, some have interpreted this failure as an indication that the behaviour of the crystal can not be represented by that of a simple classical model, because such models are physically unrealistic. However, it will be shown that the use of such a model can indeed result in accurate predictions of both polarization and refractive index when appropriate values for the electronic polarizabilities of the ions are adopted.

The computations in this paper are based on experimental observations and on the numerical results of theoretical analysis which generally may not be accurate to more than three significant figures. However, once those values are adopted for the setting up of the model, they are perfectly definite for the model, and so rather more figures than three are carried through the calculations which follow. This is so that the accuracy of the calculations for the model may not degrade during the computational procedures involved. At the stage when the final results for the model are applied to the real crystal, the additional figures may be discarded.

In what follows, polarization will be considered as arising from two causes, namely from that of the relative positions of the ionic charges within the unit cell, and from the dipoles created by the nuclear and electronic charges of the ions. It might be desirable to name these polarizations after the entities which are polarized, so that they would be called unit cell polarization and ionic polarization respectively. However, in other papers dealing with topics similar to that dealt with here, it is more usual to use the name of the entities causing the polarization, so that the terms ionic polarization and electronic polarization have been widely used to designate these two kinds of polarization respectively. In order to avoid confusion, the designations adopted for this paper are in conformity with that usage.

The ionic polarization considered here is a result of the relative static positions of the ions in the unit cell of the barium titanate crystal in its tetragonal form. It is not a result of the application of a field from an external source, and is therefore not the result of any ionic polarizability. That term would have to be introduced if an external field capable of causing movement of the ions were to be applied to the crystal. No such field is considered in this paper, which therefore is concerned with ionic polarization, but not with ionic polarizability.

It is common to say that ionic polarization is caused by the displacement or movement of ions from the positions they occupy in the cubic phase to those they occupy in the tetragonal phase. It is not strictly correct to say so, because ionic polarization is not caused by the displacement or movement of ions, but by their relative positions in the tetragonal crystal. The polarization caused by their charges would be just the same even if the crystal had no phase other than tetragonal, so that the ions would never have moved at all. Nevertheless, the displacement concept is so useful as an aid to calculation that it is employed here, but a caution must be given that it
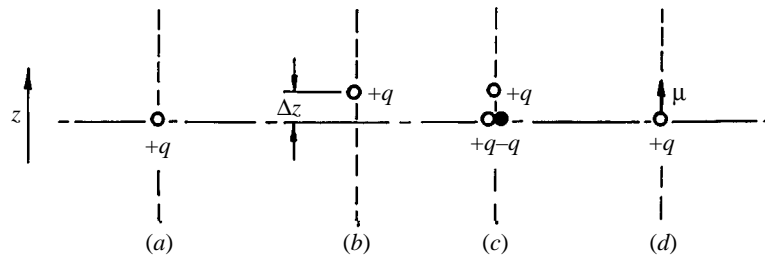
Figure 2. A charge $+q$ is shown at a lattice point in ($a$). It is displaced by a distance $+\Delta z$ in ($b$). Two charges of equal magnitude $q$ but having opposite signs are placed at the lattice point in ($c$). The displaced charge can thus be represented as a charge $+q$ at the lattice point carrying a dipole of moment $+q\Delta z$, as in ($d$).

encourages the tendency to endow the notional dipole associated with the concept of displacement with a reality that it does not possess. Thus it might have played a part in the acceptance as real of the illusory fields discussed in § 3.

## 2. Calculation of the polarization caused by displacement of ionic charges

Taking a point-charge model of an ideal single crystal in the cubic phase (figure 1$a$), it is obvious from considerations of symmetry that in the absence of an applied field the polarization is zero. An ion of such a crystal, say positive having a charge $+q$, is shown in figure 2$a$. On transition to the tetragonal phase, it moves a distance $\Delta z$ as shown in figure 2$b$. Now suppose that at the lattice point which the ion has vacated, a charge having the same sign and magnitude is notionally placed, together with another charge which only differs from the first in being of opposite sign (figure 2$c$); this notional operation has not caused any change in the resultant charge distribution from that of figure 2$b$. The charge system of figure 2$c$ is equivalent to the system shown in figure 2$d$, where the original ion is back at its initial lattice point, accompanied by a dipole having a moment $\mu$ of magnitude $q\Delta z$. The sum of such dipole moments per unit volume caused by all of the species of ion in the crystal gives the polarization $P_q$ due to charge displacement.

From the foregoing, it is evident that the ionic dipole moment per unit cell, $\mu_q$, caused by ionic charge displacement, is given by

$$\mu_q = \sum_{1}^{5} \mu_{qk} = \sum_{1}^{5} q_k \Delta z_k. \tag{2.1}$$

The absolute values of $\Delta z_k$ in the room frame of reference are not known, as experimentation only reveals the relative positions of the ions. It is conventional to imagine that the barium ion remains fixed, i.e. that $\Delta z_1$ is zero, and to assign values for $\Delta z_k$ accordingly; these $\Delta z_k$ values are then inserted into equation (2.1) to give $\mu_q$. However, if in fact the barium ion has moved a distance $\zeta$, then the equation for $\mu_q$ becomes

$$\mu_q = \sum_{1}^{5} q_k (\Delta z_k + \zeta), \tag{2.2}$$

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$$\implies \qquad \mu_q = \sum_1^5 q_k \Delta z_k + \zeta \sum_1^5 q_k. \qquad (2.3)$$

However, because the unit cell is electrically neutral

$$\sum_1^5 q_k = 0 \qquad (2.4)$$

and so equation (2.1) remains valid for the dipole moment per unit cell caused by the displacement of ionic charges no matter which ion is imagined to be fixed, or more generally, whatever fixed frame of reference is chosen.

This point is of some importance because it serves to emphasize that, by virtue of the relative displacements of its constituent ionic charges, it is only the unit cell which possesses an ionic dipole moment and not the ions themselves. The individual components of the summation on the right-hand side of equation (2.2) can have any values, dependent on the arbitrary choice of the frame of reference in which the individual ionic displacements are measured. However, the sum of these components always remains the same.

Earlier calculations have often been based on the presumption that an ion in a tetragonal crystal has a dipole moment consisting of two components, the first arising from the displacement of its charge from the position that it occupied in the cubic phase and the second from the distortion of its electron cloud, i.e. electronic polarization, and that their sum, which is taken to be a definite quantity, gives the total dipole moment of the ion; it is that total moment which has then been used to determine the dipolar electric field due to the ion. That step is quite erroneous, because although it is true that each ion does possess a definite dipole moment arising from its electronic polarizability, no meaning relating to an individual ion can be attached to the first component because $\zeta$ can have any value. The displacement of the electronic cloud of an ion causes the ion to have electronic polarization, and the displacement of ionic charges in a unit cell causes the unit cell to have ionic polarization. However, the latter polarization can not be divided into components attributable to the individual ions of the unit cell, for it arises from the displacements of the ions relative to each other.

Nevertheless, the important formative papers on the subject usually do derive a total polarizability for each ion made up of ionic and electronic components, and use the resulting dipole moment as the basis for their field calculations. For example, in his pioneering paper on the subject, Slater (1950), who considered the displacement of only the Ti ion, postulates that an ion itself has both kinds of polarizability. He introduces the notion of the ionic polarizability of ions, and in fact concludes (p. 757, col. 2) 'that the Ti ions contribute about 37% of the total polarization (of which about 31% comes from ionic displacement, 6% from electronic polarization)'. Later, in a related paper, Triebwasser (1957), who considered the displacements of all the ions, also postulates the ionic polarization of the individual ions of $BaTiO_3$, on the basis that the barium ion is undisplaced, and he lists the ionic and electronic polarizabilities of each ion in his table 1. However, he was aware of the objections that could be levelled against this procedure. He points out that 'we can anchor some other point in the cell and arrive at different results', but goes on to say in justification that 'observations ... indicate that one can really say physically that the Ba atoms are not strongly affected by the ferroelectric transition'. It will be shown

Table 1. *The charges $q_k$ (C) on the ions, taking account of electron donation from the oxygen ions to the titanium ions, and their displacements $\Delta z_k$ (m) relative to the barium ion*

| | $k$th ion | | | | |
|---|---|---|---|---|---|
| quantity | Ba | Ti | $O_a$ | $O_{b(i)}$ | $O_{b(ii)}$ |
| $q_k \times 10^{19}$ | +3.2044 | +4.6304 | −2.6116 | −2.6116 | −2.6116 |
| $\Delta z_k \times 10^{10}$ | 0 | +0.0544 | −0.1008 | −0.0617 | −0.0617 |

that even if this statement were to be true, it would still not be justifiable to add the real dipole moment due to electronic polarization to the notional dipole moment due to ionic charge displacement to give a supposed real total dipole moment of an ion.

However, it is quite permissible (q.v.) to anchor any point in the cell for the calculation of the dipole moment per cell due to ionic charge displacement within it. This dipole moment per unit cell $\mu_q$ can be calculated by means of equation (2.1), using the ionic charge values provided by Cohen & Krakauer (1990) and the ionic displacements, the barium ion taken to be fixed, given by Harada *et al.* (1970). These are given in table 1. Substitution of these values in equation (2.1) gives

$$\mu_q = 8.3741 \times 10^{-30}. \tag{2.5}$$

Now the polarization $P_q$ caused by ionic charge displacement is given by

$$P_q = \mu_q/a^3, \tag{2.6}$$

where $a$ is the length of the side of the unit cell, taken to be a cube. Taking $a$ to be $3.9920 \times 10^{-10}$ from Rhodes (1951) gives

$$P_q = 0.13164. \tag{2.7}$$

Thus ionic polarization accounts for about one-half of the experimental value of polarization $P$, namely 0.261. The electronic polarization is expected to account for the other half. To calculate that, it is necessary to know the field existing at each ion.

## 3. Calculation of the fields at ions caused by ionic charge displacement

### (*a*) *Application of the generalized Lorentz formula*

If we consider an indefinitely large cubic lattice having a unit cube with sides of length $a$ parallel to the $x$, $y$, $z$ directions, and having at each lattice point $L$ a point dipole of moment $\mu$ in the $+z$ direction, then the dipole moment per unit volume is $\mu/a^3$. The material constituted by these dipoles therefore has a polarization $P$ in the $+z$ direction given by $\mu/a^3$. It follows from the classical analysis of Lorentz (1952) that the electric field at each dipole caused by all the other dipoles is in the $+z$ direction and is given by $P/(3\epsilon_0)$, where $\epsilon_0$ is the permittivity of free space.

The Lorentz expression can be used directly to give the field created at a given ion by the dipoles of the other ions of the same species in the single crystal of barium

Table 2. *The position of each ion in the cubic lattices of each of the other ions*

($L$, lattice point, $C$, cube centre, $F_{\mathrm{h}}$, centre of horizontal face, $F_{\mathrm{v}}$, centre of vertical face, $E_{\mathrm{h}}$, centre of horizontal edge, $E_{\mathrm{v}}$, centre of vertical edge.)

| | ion | | | | |
|---|---|---|---|---|---|
| ref. lattice | Ba | Ti | $O_a$ | $O_{b(\mathrm{i})}$ | $O_{b(\mathrm{ii})}$ |
| Ba | $L$ | $C$ | $F_{\mathrm{h}}$ | $F_{\mathrm{v}}$ | $F_{\mathrm{v}}$ |
| Ti | $C$ | $L$ | $E_{\mathrm{v}}$ | $E_{\mathrm{h}}$ | $E_{\mathrm{h}}$ |
| $O_a$ | $F_{\mathrm{h}}$ | $E_{\mathrm{v}}$ | $L$ | $F_{\mathrm{v}}$ | $F_{\mathrm{v}}$ |
| $O_{b(\mathrm{i})}$ | $F_{\mathrm{v}}$ | $E_{\mathrm{h}}$ | $F_{\mathrm{v}}$ | $L$ | $F_{\mathrm{h}}$ |
| $O_{b(\mathrm{ii})}$ | $F_{\mathrm{v}}$ | $E_{\mathrm{h}}$ | $F_{\mathrm{v}}$ | $F_{\mathrm{h}}$ | $L$ |

titanate. However, to find the field caused at that ion by the dipoles of the ions of a second species, it is necessary to establish the location occupied by the first ion in the lattice of the second species. It is convenient to refer to the $x$ and $y$ directions as horizontal and the $z$ direction as vertical. Then the significant locations are the centre $C$ of the cube, the centre $F_{\mathrm{h}}$ of a horizontal face, the centre $F_{\mathrm{v}}$ of a vertical face, the centre $E_{\mathrm{h}}$ of a horizontal edge, and the centre $E_{\mathrm{v}}$ of a vertical edge. Reference to figure 1$a$ facilitates the determination of which of these points are occupied by each ionic species when each species in turn determines the reference lattice. The outcome of this consideration is given in table 2; it shows the expected diagonal symmetry.

For a single cubic lattice having at each lattice point a dipole of moment $\mu$ in the $+z$ direction, the total field $E$ in the $+z$ direction at a point other than a lattice point, and at a lattice point taking no account of the dipole at that lattice point, is given by a generalization of the Lorentz expression,

$$E = \{1/(3\epsilon_0) + S(x, y, z)\}P, \tag{3.1}$$

where the origin is at a lattice point.

The numerical value of $S(x, y, z)$ for certain special points in the unit cube of a single cubic lattice, including all of the points appearing in table 2, were evaluated by Luttinger & Tisza (1946). There were some misprints in their table of values, which were pointed out by McKeehan (1947); he himself had earlier (1933) published related work in connection with magnetic crystals. The corrected values were used by Slater (1950); they are also quoted in the book by Jona & Shirane (1962). The $S$ values given in those sources are quoted in non-rationalized Gaussian units, but they have been transformed into SI units with dimension $\mathrm{F}^{-1}$ m for display in table 3, where they are related to the points specified in table 2. The ratio of the field at those points to that at the lattice point $L$ is also shown in table 3. Inspection of table 3 shows that the broad variation in field with position is in conformity with our intuitive expectations.

### ($b$) *Principle of the calculation*

At first sight it might appear that to find the field at any ion due to ionic charge displacements, all that would be necessary would be to find the component of field caused by the displacement of each species of ion by using equation (3.1) with the appropriate $S$ value taken from table 3 chosen with reference to table 2, and then

Table 3. *The S factor* ($F^{-1}$ m) *related to some special points (see table 2) in a cubic lattice for the determination of the field E existing at them according to the generalized Lorentz expression (equation (3.1)), and the ratio of E to the field $E_L$ at the lattice points*

|  |  |  | point | | | |
|---|---|---|---|---|---|---|
|  | $L$ | $C$ | $F_{\mathrm{h}}$ | $F_{\mathrm{v}}$ | $E_{\mathrm{h}}$ | $E_{\mathrm{v}}$ |
| $S \times 10^{-9}$ | 0 | 0 | $-77.904$ | $+38.952$ | $-135.172$ | $+270.345$ |
| $E/E_L$ | $+1$ | $+1$ | $-1.069$ | $+2.035$ | $-2.591$ | $+8.181$ |

to sum the five results. There is, however, a difficulty. We need to know the value of $P$ for each of the five interpenetrating lattices in order to insert it in equation (3.1). This means that we need to evaluate the dipole moment associated with the displacement of each ionic charge. But we know from the argument of § 2 that while the sum of such dipole moments within the unit cell has meaning (see equations (2.3) and (2.4)), no individual value for dipole moment due to its charge displacement can be assigned to any ion, since $\zeta$ can be given any value we choose. While any value of $\zeta$ would result in the same value for the dipole moment $\mu_q$ of the unit cell caused by ionic charge displacement (q.v.), there is no corresponding identity of results for different values of $\zeta$ in the case of the calculation of the field resulting from the summation of the five $E$ values derived from equation (3.1). The reason is that a given change in $\zeta$ will change the fields at the special points by different amounts, as is evident from the lower row in table 3. The fields at these points have different comparative weightings in the determination of the total field at each ion, as can be seen by inspection of the columns of table 2. The result obtained for the total field at an ion owing to ionic charge displacement will therefore depend upon the choice of the value of $\zeta$. Up to now it has been the practice to take the barium ions to be fixed, i.e. to take $\zeta$ to be equal to zero. There is however no reason to suppose that this value is more appropriate than any other arbitrary value. Some further consideration is required concerning the factors that should govern the choice of the value of $\zeta$.

The consideration is helped by taking notice of what appears to be a curious anomaly. Part of a cross-section in the $yz$ plane through identical positive ions each with charge $+q$ arranged in an indefinitely large cubic lattice is shown in figure 3a. It is obvious from considerations of symmetry that there is no electric field at, and therefore no force acting on, any ion. Now following a procedure similar to that illustrated in figure 2, the ions are all supposed to be displaced by a distance $\Delta z$, as shown in figure 3b. The positions of the ions relative to each other is unchanged, and again there is no field at, or force on, any ion. Following the principle explained in § 2, the displaced ions can be represented by ions notionally restored to their original positions, and the charge system of figure 3b is equivalent to that of figure 3c, in which each charge $+q$ is accompanied by a dipole of magnitude $+q\Delta z$. There thus appears to be a field acting on each ion given by the Lorentz expression, and the whole array therefore apparently accelerates away in the $+z$ direction. That is a proposition which would have astonished Newton, on account of his Third Law.

There is of course a flaw in the reasoning leading to that absurd conclusion. It is evident even without recourse to Newton that the system of figure 3b is electrically
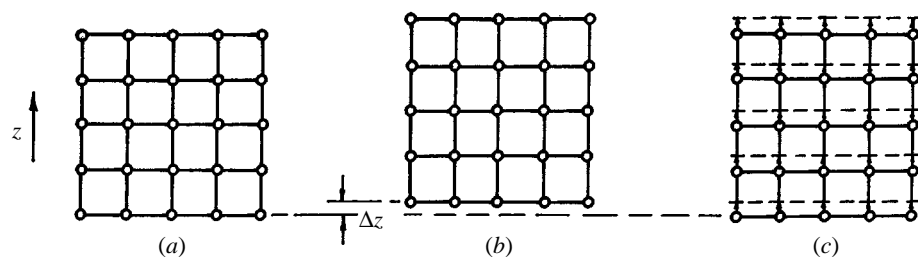
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Figure 3. A cubic lattice of positive ions of charge $+q$ is shown in $(a)$. It is displaced by a distance $+\Delta z$ in $(b)$. In $(c)$, the displaced ions are represented by ions at their original lattice points, each carrying a dipole of moment $+q\Delta z$.

identical to that of figure $3a$, and that the notional restoration of the ions to their original positions can not conjure up fields and forces. This seems so obvious that it might be thought that there is no need to labour the point, or even to mention it. Yet the apparent fields at the lattice points shown in figure $3c$ have been taken as real and included in the previously mentioned important formative papers in the subject. For example, in the paper by Slater (1950), the field at the Ti ion has a component which is attributed to the movement of the array of Ti ions (see his eqn (31)), i.e. the field supposedly existing in figure $3c$ is taken as real. This mistaken notion, subsequently taken up by other investigators, e.g. eqn (2) of Triebwasser (1957), stems from the earlier misconception discussed in §2, namely that each ion has its own real ionic dipole moment caused by its displacement. From there, the next step is to attribute a real field to the presumed real dipole arising from the displacement of each ion, and that leads to erroneous field calculations. Measured ionic displacements are relative, and individual ionic displacement figures have no meaning taken in isolation.

The resultant field $E_{qk}$ at the $k$th ion due to ionic charge displacements is given by the sum of the fields $E_{qjk}$ caused by the displacements of species of ion having the designation $j$. From the foregoing, it is clear that especial care has to be taken not to include any illusory component $E_{qkk}$ attributable to the displacement of ions of the $k$th species. The exclusion of such components can be ensured by always choosing as reference the lattice of the ion at which the field is being calculated. In that way, the ion will be deemed to have no displacement, and therefore have no notional dipole moment and set up no field arising from displacement; the only field it experiences owing to ionic displacement arises from the displacement relative to itself of other species of ions. This procedure implies that a given ion will have different values of displacement depending upon at which ion the field is being calculated. That does not matter, although the relative shifts of the different species of ion must remain fixed, no matter which species of ion provides the reference lattice. The fields arising from ionic displacement will now be calculated on that basis.

### ($c$) *Results of the calculation*

To illustrate the implementation of the proposed procedure, the example will be given of the calculation of the field $E_{q32}$ at the Ti ions caused by the displacement of the charges of the $O_a$ ions. The steps are as follows.

(i) In order to take the Ti lattice as reference, $0.0544 \times 10^{-10}$ is subtracted from each of the values given in the last row of table 1. For the $O_a$ ion, the displacement becomes $-0.1552 \times 10^{-10}$.

(ii) To find the notional dipole moment $\mu_{qk}$ caused by the displacement of each ionic charge, its displacement referred to the Ti lattice is multiplied by the charge, given in the first row of table 1. For the $O_a$ ion, $\mu_{q3} = +4.0532 \times 10^{-30}$.

(iii) To find the notional polarization $P_{qk}$ caused by the displacement of each ionic charge, $\mu_{qk}$ is divided by $a^3$. For the $O_a$ ion, $P_{q3} = 0.0637$.

(iv) The relevant special point is found from table 2. For the Ti ion in the $O_a$ lattice, it is $E_v$.

(v) The corresponding $S$ value is found from table 3. For $E_v$ it is $+270.345 \times 10^9$.

(vi) The values of $P_{qk}$ and $S$ are substituted in equation (3.1) to give the field $E_{q32}$ at the Ti ions caused by the displacement of the charge of the $O_a$ ions. The result is $+19.623 \times 10^9$.

This process is repeated to find the field at the Ti ions caused by the displacements of the charges of the Ba, $O_{b(i)}$ and $O_{b(ii)}$ ions, and the four fields are added to give the total field $E_{q2}$ at the Ti ion caused by ionic charge displacements. In the above example, the dipole moment $\mu_{q3}$ and the resulting polarization $P_{q3}$ caused by the displacement of the $O_a$ ion are both described as 'notional' because when the field created at an ion other than the Ti ion by the displacement of the charge of the $O_a$ ion is considered, that displacement in the lattice of the other ion taken as the frame of reference will be different, and so give rise to different values for $\mu_{q3}$ and $P_{q3}$. That is why these quantities can only be described as notional. Nevertheless, in the particular case of the example above, the notional dipoles are caused by the true displacement of the charges of the $O_a$ ions relative to the Ti ions, and so the resulting field $E_{q32}$ has a real, not a notional, magnitude. Thus, unlike the calculation for ionic polarization discussed in §2 for which five components without individual meaning sum to give a total with meaning, each of the four fields $E_{qjk}$ which sum to give the total field $E_{qk}$ at each ion caused by ionic displacement has its own real individual magnitude. It is therefore quite permissible to refer to, for example, the field created at the Ti ions by the displacement relative to them of the charges of the $O_a$ ions; it is a real field with a definite magnitude, and it gives rise to an electrostatic force of definite magnitude $q_2 E_{q32}$ on the charge of each Ti ion.

The whole procedure is then repeated to find the fields at the other ions resulting from the ionic charge displacements relative to them; the results are shown in table 4a. For comparison, the results obtained using the conventional procedure in which the barium lattice is taken as reference throughout the whole calculation, i.e. the displacement values are fixed at those given in table 1, are shown in table 4b. There are marked differences between the field values shown in tables 4a and 4b.

The electrostatic force experienced by each ion caused by the fields resulting from ionic charge displacement is obtained by multiplying the fields in table 4a, and for the sake of comparison in table 4b, by the appropriate ionic charges. The results are shown in tables 5a and 5b. The difference between these tables is even more striking. Table 5a, with its diagonal symmetry of quantities of opposite signs, shows clearly that the forces predicted are in conformity with Newton's Third Law, and that ionic charge displacement causes zero electrostatic force on the unit cube. That is not so for the quantities shown in table 5b. Summation of the forces in the bottom row shows that a resultant force is predicted on the unit cube of $+1.2822 \times 10^{-9}$, a force quite comparable with that on the Ba or $O_b$ ion.

It was to be expected that there would be a resultant force, because of the inclusion of the illusory forces to which reference has already been made. However, if all these are discounted by putting a zero in table 5b in all the places where a zero appears

Table 4. *The field $E_{qjk}$ (V m$^{-1}$) at each kth ion caused by the charges of all of the jth ions*

(Field calculated according to (*a*) the displacements relative to the *k*th ion of all other ions and (*b*) the displacements of all ions, including the *k*th ions, relative to that of the barium ion. These fields total $E_{qk}$ at each *k*th ion.)

(*a*)

| | field $\times 10^{-9}$ *k*th ion | | | | |
|---|---|---|---|---|---|
| *j*th ion | Ba | Ti | $O_a$ | $O_{b(i)}$ | $O_{b(ii)}$ |
| Ba | 0 | −1.0316 | −2.0440 | +2.3806 | +2.3806 |
| Ti | +1.4906 | 0 | +34.7919 | −8.2413 | −8.2413 |
| $O_a$ | −1.6659 | +19.6230 | 0 | +1.2295 | +1.2295 |
| $O_{b(i)}$ | +1.9402 | −4.6482 | −1.2295 | 0 | 0 |
| $O_{b(ii)}$ | +1.9402 | −4.6482 | −1.2295 | 0 | 0 |
| total | +3.7051 | +9.2950 | +30.2889 | −4.6312 | −4.6312 |

(*b*)

| | field $\times 10^{-9}$ *k*th ion | | | | |
|---|---|---|---|---|---|
| *j*th ion | Ba | Ti | $O_a$ | $O_{b(i)}$ | $O_{b(ii)}$ |
| Ba | 0 | 0 | 0 | 0 | 0 |
| Ti | +1.4906 | +1.4906 | +12.1951 | −3.8616 | −3.8616 |
| $O_a$ | −1.6659 | +12.7448 | +1.5578 | +3.1697 | +3.1697 |
| $O_{b(i)}$ | +1.9402 | −2.4702 | +1.9402 | +0.9536 | −1.0197 |
| $O_{b(ii)}$ | +1.9402 | −2.4702 | +1.9402 | −1.0197 | +0.9536 |
| total | +3.7051 | +9.2950 | +17.6333 | −0.7580 | −0.7580 |

in table 5*a*, the predicted resultant force due to ionic charge displacement would not disappear, but would in fact increase to $+1.4968 \times 10^{-9}$. It is clear that there is a defect in the conventional procedure in addition to the inclusion of the self-generated illusory forces. A better understanding of the defects of the conventional procedure is necessary; this will be pursued in § 4.

## 4. Calculation of the electrostatic force between ions possessing dipoles

### (*a*) Derivation of a compensation factor

Two ions of the model are shown in figure 4*a*. They have charges $q_j$ and $q_k$ and electronic dipoles of moment $\mu_{ej}$ and $\mu_{ek}$ respectively; their horizontal separation is $r$, and their vertical separation is $z$, taken as positive for the ion of the *k*th species above that of the *j*th species. The dipole moments $\mu_{ej}$ and $\mu_{ek}$ will both be taken to be positive, i.e. directed upwards, as indeed will be later shown to be the case for

Table 5. *The force $F_{qjk}$ (N) on the charge of each $k$th ion caused by the charges of all of the $j$th ions*

(Force calculated according to ($a$) the displacements relative to the $k$th ions of all other ions and ($b$) the displacements of all ions, including the $k$th ions, relative to that of the barium ion. These forces total $F_{qk}$ on each $k$th ion.)

($a$)

| | force $\times 10^9$ $k$th ion | | | | |
|---|---|---|---|---|---|
| $j$th ion | Ba | Ti | $O_a$ | $O_{b(i)}$ | $O_{b(ii)}$ |
| Ba | 0 | $-0.4777$ | $+0.5338$ | $-0.6217$ | $-0.6217$ |
| Ti | $+0.4777$ | 0 | $-9.0862$ | $+2.1523$ | $+2.1523$ |
| $O_a$ | $-0.5338$ | $+9.0862$ | 0 | $-0.3211$ | $-0.3211$ |
| $O_{b(i)}$ | $+0.6217$ | $-2.1523$ | $+0.3211$ | 0 | 0 |
| $O_{b(ii)}$ | $+0.6217$ | $-2.1523$ | $+0.3211$ | 0 | 0 |
| total | $+1.1873$ | $+4.3039$ | $-7.9102$ | $+1.2095$ | $+1.2095$ |

($b$)

| | force $\times 10^9$ $k$th ion | | | | |
|---|---|---|---|---|---|
| $j$th ion | Ba | Ti | $O_a$ | $O_{b(i)}$ | $O_{b(ii)}$ |
| Ba | 0 | 0 | 0 | 0 | 0 |
| Ti | $+0.4777$ | $+0.6902$ | $-3.1849$ | $+1.0085$ | $+1.0085$ |
| $O_a$ | $-0.5338$ | $+5.9014$ | $-0.4068$ | $-0.8278$ | $-0.8278$ |
| $O_{b(i)}$ | $+0.6217$ | $-1.1438$ | $-0.5067$ | $-0.2490$ | $+0.2663$ |
| $O_{b(ii)}$ | $+0.6217$ | $-1.1438$ | $-0.5067$ | $+0.2663$ | $-0.2490$ |
| total | $+1.1873$ | $+4.3040$ | $-4.6051$ | $+0.1980$ | $+0.1980$ |

the electronic dipoles of all of the ions of the model. The vertical component of the electrostatic force exerted on the $k$th ion by the $j$th ion will now be calculated.

That force has four components, which are easily found by means of elementary electrostatics to be given by the following expressions:

$$\text{(i) Vertical force on } q_k \text{ caused by } q_j = \frac{q_j q_k z}{4\pi\epsilon_o (z^2 + r^2)^{3/2}}. \tag{4.1}$$

$$\text{(ii) Vertical force on } q_k \text{ caused by } \mu_{ej} = \frac{\mu_{ej} q_k (2z^2 - r^2)}{4\pi\epsilon_0 (z^2 + r^2)^{5/2}}. \tag{4.2}$$

$$\text{(iii) Vertical force on } \mu_{ek} \text{ caused by } q_j = -\frac{\mu_{ek} q_j (2z^2 - r^2)}{4\pi\epsilon_0 (z^2 + r^2)^{5/2}}. \tag{4.3}$$

$$\text{(iv) Vertical force on } \mu_{ek} \text{ caused by } \mu_{ej} = -\frac{3\mu_{ej}\mu_{ek} z (2z^2 - 3r^2)}{4\pi\epsilon_0 (z^2 + r^2)^{7/2}}. \tag{4.4}$$
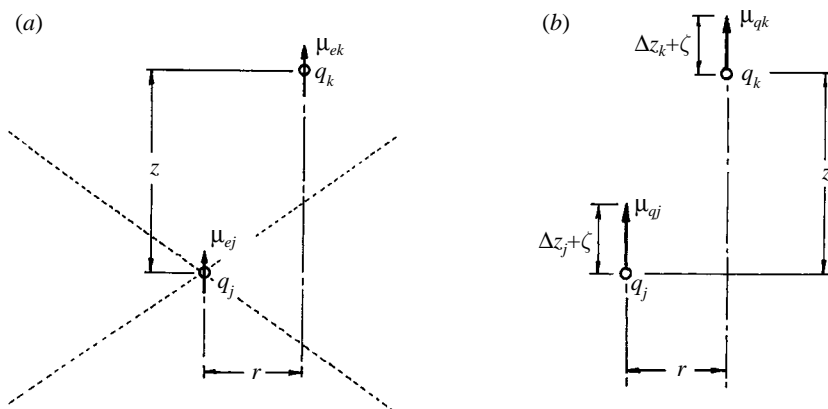
*J. H. Calderwood*



Figure 4. Two single ions of the $j$th and $k$th species ($a$) with electronic dipoles. The vertical component of the field caused by the dipole of the former is positive inside, and negative outside, the cones represented by the dotted lines, and ($b$) with notional dipoles arising from ionic displacement.

For the calculation of the fields and forces due to the charges of the ions, the fact that they occupy the sites shown in figure 1$b$, rather than those of figure 1$a$, was taken into account by the device of the introduction of notional dipoles, the ions being restored to the tetragonal lattice points of figure 1$b$. Thereafter, the unit cell was treated as a cube, and the position of the ions, with their notional and real dipoles, was taken to be that shown in figure 1$a$. From then on, the restored ions did not feature in the analysis. The force given by equation (4.1) is that caused on one restored charge by another. We know from symmetry that if the fields caused at the restored charge by all other restored charges were to be added, the result must be zero, and so the force on the restored charge must be zero also. That is indeed the prediction of equation (4.1), since in the vertical line through the ion of the $j$th species shown, for every ion having a position designated by $+z_n$, there will be another having a position designated by $-z_n$, and $z$ is a multiplier of the right-hand side of the equation. This argument may be applied to all ions of whatever species situated on a vertical line, and so the total vertical force on the charge of the restored ion of the $k$th species caused by the fields of the charges of all other ions is analytically confirmed to be zero. Since $z$ is also a multipler of the right-hand side of equation (4.4), a similar argument holds, and the total vertical force on the dipole of the ion of the $k$th species caused by the fields of the dipoles of all other ions of the crystal is also zero. Although it has not been shown analytically here, it is evident from symmetry that there is also no component of force in any horizontal direction on any ion.

Coming now to the force given by equation (4.2), it is evident that the total vertical force on $q_k$ caused by the fields of the dipoles of all other ions will not be zero. If we imagine two cones, one of them being inverted, having the same vertical axis, with semi-vertical angle $\arctan \sqrt{2}$ (about $55°$), each with its apex at the ion of the $j$th species, then from elementary electrostatics the vertical component of the field of $\mu_{ej}$ is positive at all points inside those cones, and negative everywhere else, except on the surface of the cones where it is zero. Hence the vertical field at the charge $q_k$ caused by the field of $\mu_{ej}$ is in the $+z$ direction if $2z^2 > r^2$ and in the $-z$ direction if $2z^2 < r^2$, i.e. the vertical field changes direction when $z$ is $\pm r/\sqrt{2}$, as is also evident

from equation (4.2). The vertical fields $E_{\mathrm{e}jk}$ at $q_k$ caused by the dipoles of all of the $j$th species of ion may be found by the use of the method already described in § 3 which employs the generalized formula of Lorentz. This method will be used in § 5 to give the total field $E_{\mathrm{e}k}$, i.e. that field at the ions of the $k$th species caused by the electronic polarization of all other ions, which when added to the field $E_{qk}$ gives the total field $E_k$ responsible for the electronic polarization of ions of the $k$th species.

There remains the force given by equation (4.3). It arises from the fact that the charge $q_j$ creates a different field at each of the dipolar charges of the ion of the $k$th species being considered, and so there is a net force on its dipole. Combining this force with that given by equation (4.2) gives the vertical force $F$ caused by the dipole and charge of the single ion of the $j$th species acting on the charge and dipole respectively of the single ion of the $k$th species shown in figure $4a$ to be

$$F = \frac{2z^2 - r^2}{4\pi\epsilon_0(z^2 + r^2)^{5/2}}(\mu_{\mathrm{e}j}q_k - \mu_{\mathrm{e}k}q_j). \qquad (4.5)$$

Here the term in $\mu_{\mathrm{e}j}q_k$ gives the force on $q_k$ caused by the field of $\mu_{\mathrm{e}j}$ at the lattice point occupied by $q_k$, while that in $\mu_{\mathrm{e}k}q_j$ is the net force on the charges of the dipole $\mu_{\mathrm{e}k}$ caused by the field of $q_j$ at those charges. The existence of both of these forces is obvious when only two ions are involved; however, when the ions are arrayed in an indefinitely extended lattice, the second term is easily overlooked. That is because it arises from the forces on the charges of the dipoles, which are rarely explicitly considered. There is a tendency to imagine that the force on an ion is simply the product of the charge on that ion and the field existing at the lattice point at which both the point charge and point dipole of the ion are situated. That field from symmetry is vertical, and it might seem at first that the forces on the charges of the point dipole, which is vertically aligned and of extremely short length, cancel each other. Then only the first term of equation (4.5) would be taken into account. That term might appropriately be called the apparent force $F_{\mathrm{app}}$; it may be defined as that component of the electrostatic force on an ion caused by the field of the dipoles of other ions acting on its charge.

Since the apparent force $F_{\mathrm{app}}$ may be readily calculated, it is expedient to rewrite equation (4.5) as

$$F = \frac{\mu_{\mathrm{e}j}q_k(2z^2 - r^2)}{4\pi\epsilon_0(z^2 + r^2)^{5/2}}\left[1 - \frac{\mu_{\mathrm{e}k}q_j}{\mu_{\mathrm{e}j}q_k}\right], \qquad (4.6)$$

or

$$F = F_{\mathrm{app}}C. \qquad (4.7)$$

Here $C$ is a compensation factor by which the apparent force $F_{\mathrm{app}}$ must be multiplied to give the true force $F$. It only applies if the two dipole moments are directed along coincident or parallel lines, $F_{\mathrm{app}}$ and $F$ being the force components resolved in their direction.

The compensation factor $C$ was derived by a consideration of only two ions, their relative positions being determined by the quantities $z$ and $r$. However, these quantities do not appear in the expression for $C$ derived from equation (4.6), so that the compensation factor $C$ is the same whatever their values, and can be written $C_{\mathrm{e}jk}$ to indicate that it can be used in the calculation of the net force caused by any $j$th ion on any $k$th ion due to the action of $\mu_{\mathrm{e}j}$ on $q_k$ and of $q_j$ on $\mu_{\mathrm{e}k}$. From equations

(4.6) and (4.7) we have

$$C_{\mathrm{e}jk} = 1 - \frac{\mu_{\mathrm{e}k}q_j}{\mu_{\mathrm{e}j}q_k}. \tag{4.8}$$

It follows that in the summation process to find the force $F_{\mathrm{e}jk}$ on any ion of the $k$th species given by the sum of the forces caused by (i) the sum $E_{\mathrm{e}jk}$ of the fields of the dipoles of all the $j$th ions acting on the charge of the $k$th ion and (ii) the sum of the fields of the charges of all the $j$th ions acting on the charges of the dipoles of the $k$th ion, it is only necessary to calculate the former forces, using the generalized Lorentz formula. The result can then be multiplied by $C_{\mathrm{e}jk}$ to obtain the sum $F_{\mathrm{e}jk}$ of the forces in categories (i) and (ii) above. This procedure is then repeated for $j$ taking all values from 1 to 5, including the value of $k$, using the appropriate value for $C_{\mathrm{e}jk}$ in each case; the results are summed to give $F_{\mathrm{e}k}$. The reason for the inclusion of the $j = k$ value is to ensure that the value of $E_{\mathrm{e}kk}$ is recorded; it is evident from equation (4.8) that when $j = k$, $C_{\mathrm{e}kk} = 0$ so that for ions of the same species the net force $F_{\mathrm{e}kk}$ due to dipole–charge and charge–dipole interaction is given analytically as zero; however, the field $E_{\mathrm{e}kk}$ is not zero. The final step is to add the force $F_{qk}$ due to the field of the displaced ionic charges acting on $q_k$, which has already been calculated in §3 $c$ and is presented in table 4$a$, to find the total electrostatic force $F_k$ on each of the ions of the $k$th species.

The force $F_{\mathrm{e}jk}$ is given by the product $C_{\mathrm{e}jk}E_{\mathrm{e}jk}q_k$. It is convenient to consider $C_{\mathrm{e}jk}E_{\mathrm{e}jk}$ to be a notional force-field $E_{\mathrm{ce}jk}$ which is imagined to act on the charge $q_k$ to give directly the force $F_{\mathrm{e}jk}$ acting on the $k$th ions, so that $F_{\mathrm{e}jk}$ can be written simply as $E_{\mathrm{ce}jk}q_k$. It must be emphasized that the field $E_{\mathrm{ce}jk}$ has no real existence. The force $F_{\mathrm{e}jk}$ is actually caused by three different fields acting on three charges, i.e. on $q_k$ and on those of the dipole $\mu_{\mathrm{e}k}$. The total notional force-field $E_{\mathrm{ce}k}$, which also has no real existence, imagined to act on $q_k$ to give the real force $F_{\mathrm{e}k}$, is obtained by summing the values of $E_{\mathrm{ce}jk}$.

Thus the total electrostatic field $E_k$ acting at the lattice point occupied by the $k$th ion is given by

$$E_k = E_{qk} + E_{\mathrm{e}k}. \tag{4.9}$$

It is the field $E_k$ which causes electronic polarization of the $k$th ion, so that the dipole moment $\mu_k$ of each ion of that species is given by

$$\mu_{\mathrm{e}k} = E_k\alpha_k, \tag{4.10}$$

where $\alpha_k$ is the electronic polarizability of the $k$th ion.

The total electrostatic force $F_k$ on the $k$th ion is given by

$$F_k = q_k(E_{qk} + E_{\mathrm{ce}k}). \tag{4.11}$$

For an indefinitely large cubic lattice of ions having identical charges and dipoles all oriented in the $+z$ direction, $C$ is zero from equation (4.8), so that $E_{\mathrm{ce}k}$ is zero. Since $E_{qk}$ is zero from symmetry, $F_k$ is zero from equation (4.11). Thus the lattice of figure 3$c$, which in §3 $b$ was denied locomotion on the grounds that no field existed at its lattice points since it was only a lattice of charges which had been displaced and restored, would still be denied self-propulsion even if it were to be furnished with real dipoles which do create a field at the lattice points. The compensation factor rightly predicts that this real field produces zero force on each ion, the physical reason being that the force on the charge of each ion is equal and opposite to the force on its dipole. Thus the electrostatic analysis agrees with Newton, as it must.

To revert to the model, the vertical force caused by the single ion of the $k$th species on that of the $j$th species shown in figure $4a$ is given by interchanging the subscripts in equation (4.5), which gives the result of $-F$; this is in accordance with Newton's Third Law. That is so for any pair of ions, and so it follows that in each unit cell of the crystal, the electrostatic forces on the charges and dipoles caused by electronic polarization of all of the ions of the crystal add to zero. The electrostatic forces on the charges of each of the ions of a unit cell caused by the charges of all of the ions of the crystal also add to zero, as was shown in §3. The total electrostatic force on the ions of each unit cell is therefore zero. However, the total electrostatic force on an individual ion, given by equation (4.11), is in general not zero.

Since the ions are all in equilibrium, it follows that each ion must be subjected to another force, equal and opposite to the electrostatic force given by equation (4.11). This balancing force is in fact made up from several other forces in the real crystal which have been discussed by Fowler & Pyper (1985). Since the sum of the electrostatic forces over all of the ions of each unit cell is zero, then so must be the sum of the balancing forces. Their origin is not incorporated in the model, which is based upon the premise that the ions are in equilibrium in known positions in the tetragonal crystal. The *ab initio* calculation of the balancing forces calls for the use of the machinery of modern theoretical physics, and is quite outside the scope of the classical point-charge/point-dipole model being analysed here.

### (b) *Application of the compensation factor to ionic charge displacement*

The fields arising from the displacement of ionic charges from their positions in the cubic structure to those in the tetragonal structure were calculated in §3 using the device of notional dipoles. The reference frame was moveable, and was always chosen as the lattice of the ion at which the field was being calculated, in order to avoid the inclusion of illusory fields and forces. The consequence of choosing a fixed frame of reference, that of the barium ion, was examined numerically, and the results relating to fields and forces are shown in table $4b$ and table $5b$ respectively.

The consequence of choosing a fixed frame of reference will now be examined analytically. We shall start by considering only two ions of the model, and shall find the field at, and the force on, the charge of a single $k$th ion caused by the charge of a single $j$th ion. In figure $4b$ the dipoles shown are notional, of length $(\Delta z_j + \zeta)$ and $(\Delta z_k + \zeta)$ determined by the ionic charge displacements, whereas in §4$a$ the dipoles were real, and determined by electronic polarization. The dipole moment $\mu_{qk}$ of the notional dipole of the $k$th ion is given by $q_k(\Delta z_k + \zeta)$, where $\Delta z_k$ is the displacement of the $k$th ion relative to the barium ion, and $\zeta$ is an arbitrary length; analogous quantities relate to the $j$th ion, $\zeta$ being unchanged.

Elementary electrostatics shows that:

$$\text{Vertical field at } q_k \text{ caused by } \mu_{qj} = \frac{q_j}{4\pi\epsilon_0} \frac{2z^2 - r^2}{(z^2 + r^2)^{5/2}} (\Delta z_j + \zeta). \tag{4.12}$$

This clearly has no unique value as $\zeta$ can have any value.

The notional apparent vertical force $F_{\text{app}}$ on the single $k$th ion is given by the above expression multiplied by $q_k$, and for the same reason, that has no unique value.

From equation (4.8),

$$C_{qjk} = 1 - \frac{\Delta z_k + \zeta}{\Delta z_j + \zeta}. \tag{4.13}$$

Substituting the above values into equation (4.7) to find the notional vertical force $F$ on the single $k$th ion gives

$$F = \frac{q_j q_k}{4\pi\epsilon_0} \frac{2z^2 - r^2}{(z^2 + r^2)^{5/2}} (\Delta z_j - \Delta z_k). \tag{4.14}$$

The two striking features of this equation are that the term $\zeta$ has vanished, and that only the difference in ionic displacements appears. The first means that $F$ has a definite value, the same for all values of $\zeta$, and therefore is real not notional. The second means that the frame of reference is fixed by the location of the $k$th ion on which the force is being calculated. The $k$th ion therefore has no notional dipole, and the effect of that (see §3$c$) is that the true force $F$, rather than an apparant force $F_{\mathrm{app}}$, results. When the right-hand side of equation (4.12) is multiplied by $q_k$ to give $F_{\mathrm{app}}$ and compared with the expression for $F$ given by equation (4.14), it is at once evident that the effect of the introduction of the compensation factor $C_{qjk}$ has been to put $\zeta = -\Delta z_k$. This ensures that the $k$th ion is undisplaced, and so the compensation factor has made certain that the $k$th ion determines the frame of reference; the calculation then proceeds in the same way as the initial calculation using a moveable frame of reference. Therefore when the force $F_{qk}$ caused by the charges of all other ions on the charges of the $k$th ions is found by summation, using the appropriate compensation factors, the results to emerge should be the values shown in table 5$a$. This will now be shown to be so.

The figures given in table 5$b$ relate to the case when the barium ion provides the fixed frame of reference throughout, i.e. $\zeta = 0$. They were obtained by multiplying the field created by the notional dipoles of a given species of ion, at the lattice points of all species of ion, by the charges of those ions. The resulting force is therefore the apparent force, and to find the true force it must be multiplied by the appropriate compensation factor. That is a simple matter, because when $\zeta$ is zero, the dipole moment $\mu_{qk}$ associated with each charge $q_k$ is given by $q_k \Delta z_k$. The compensation factor $C_{qjk}$ for the calculation of the force-field created by the $j$th ions on the $k$th ions is given by equation (4.13) which therefore becomes

$$C_{qjk} = 1 - \frac{\Delta z_k}{\Delta z_j}. \tag{4.15}$$

Values for $C_{qjk}$ obtained by the use throughout of the $\Delta z$ values given in table 1 are shown in table 6 (the figure when both $j$ and $k$ refer to Ba is indeterminate). When the figures in a given position in table 5$b$ are multiplied by the $C_{qjk}$ values in the corresponding positions of table 6, the figures of table 5$a$ do indeed result. The use of the compensation factor has thus ensured the correct result for the forces between the charges of ions of all species, and not just the prediction of zero force between the charges of ions of the same species, which is but a particular case.

These figures give the force $F_{qjk}$ on the charge $q_k$ of the $k$th ions caused by the fields $E_{qjk}$ at the $k$th ions of the charge $q_j$ of the $j$th ions. The fields $E_{qjk}$ can therefore be found by dividing $F_{qjk}$ given in table 5$a$ by the appropriate charge $q_k$ given in table 1. The values so obtained are the figures of table 4$a$, which had already been found (see §3) by the method of using a moveable frame of reference.

Thus we see that that method, and the method using a fixed frame of reference together with the compensation factor $C_{qjk}$, give identical results for the fields at, and the forces acting on, the charges of each ion caused by the charges of other ions. To find these fields and forces, the former method is the easier and the more direct.

Table 6. *Compensation factors $C_{qjk}$ calculated from equation (4.15)*

(When the figures of tables 4*b* and 5*b* are multiplied by the appropriate $C_{qjk}$ factor, the figures of tables 4*a* and 5*a* result.)

|  | | | $k$th ion | | |
| --- | --- | --- | --- | --- | --- |
| $j$th ion | Ba | Ti | $O_a$ | $O_{b(i)}$ | $O_{b(ii)}$ |
| Ba | — | $\pm\infty$ | $\pm\infty$ | $\pm\infty$ | $\pm\infty$ |
| Ti | $+1$ | $0$ | $+2.8529$ | $+2.1342$ | $+2.1342$ |
| $O_a$ | $+1$ | $+1.5397$ | $0$ | $+0.3879$ | $+0.3879$ |
| $O_{b(i)}$ | $+1$ | $+1.8817$ | $-0.6337$ | $0$ | $0$ |
| $O_{b(ii)}$ | $+1$ | $+1.8817$ | $-0.6337$ | $0$ | $0$ |

However, it is not an option when we come to consider not notional dipoles, but real dipoles which can not be reduced to zero for the convenience of calculation.

## 5. Calculation of the fields at ions caused by electronic polarization

The field at an ion caused by the electronic polarization of all other ions will be determined by means of the Lorentz expression, modified as necessary to take account of the position of the ion at which the field is being calculated in the lattices of the other ions. The calculation will follow the same procedure as that employed for the calculation of the fields $E_{qk}$ set up by the notional dipoles existing because the charges of the displaced ions in the tetragonal phase had been notionally restored to the lattice points they occupy when the crystal is in the cubic phase. We shall again treat the crystal as being cubic, and shall take it that the real dipoles $\mu_{ek}$ caused by electronic polarization have been restored to the lattice points as constituent parts of the restored ions.

Since the dipole moment $\mu_{ej}$ associated with the electronic cloud of the $j$th ion is given by $\alpha_j E_j$, the resulting component $P_{ej}$ of electronic polarization is given by

$$P_{ej} = \alpha_j E_j / a^3, \tag{5.1}$$

where $E_j$ is the total electrostatic field, caused by both ionic charges and electronic polarization, appearing at the lattice points occupied by the model ions of the $j$th species. Hence the field $E_{ejk}$ at the lattice points occupied by the model ions of the $k$th species created by the array of dipoles $\mu_{ej}$ is given by the substitution of the appropriate values of $S_{jk}$ and $P_{ej}$ in equation (3.1). It follows that the total electrostatic field $E_k$ at those lattice points occupied by ions of the $k$th species is given by

$$E_k = E_{qk} + \sum_{j=1}^{5} E_{ejk}. \tag{5.2}$$

It should be noticed that $j$ takes all values between 1 and 5 inclusive in this equation, including that for which $j = k$.

Substitution of appropriate values in equation (5.2) gives five simultaneous equations for the total electrostatic fields at the ions, $E_1$, $E_2$, $E_3$, $E_4$, $E_5$. Values for $E_{qk}$

have already been calculated in §3, but for the calculation of the fields $E_k$ it is necessary to know the magnitudes of the electronic polarizabilities $\alpha_k$. These magnitudes are not known with certainty, and so they will be carried as symbols throughout the calculation. In order to avoid many repetitions of the factor $10^{-40}$, we shall write

$$\mathcal{A}_k \equiv \alpha_k \times 10^{40}, \qquad \mathcal{M}_k \equiv \mu_{\mathrm{e}k} \times 10^{40}. \tag{5.3}$$

The decision to carry $\mathcal{A}_k$ symbolically means that the right-hand side of equations derived from equation (5.2) will contain, in all terms except the first, products $\mathcal{A}_k E_k$, and so they are conveniently written in terms of $\mathcal{M}_k$. The left-hand side of those equations can also conveniently be written in terms of $\mathcal{M}_k$, since $E_k$ is given by $\mathcal{M}_k/\mathcal{A}_k$. The five simultaneous equations can then be solved for $\mathcal{M}_k$, and so solutions for $E_k$ can be obtained in terms of $\mathcal{A}_1, \mathcal{A}_2, \mathcal{A}_3, \mathcal{A}_4, \mathcal{A}_5$.

Implementation of the above procedure yields the following five simultaneous equations relating the quantities $\mathcal{A}_k$ and $\mathcal{M}_k$ (the coefficients in these equations, and others to follow, in general are not pure numbers):

$$\mathcal{M}_1/\mathcal{A}_1 = +3.7051 \times 10^9 + 0.05918\mathcal{M}_1 + 0.05918\mathcal{M}_2$$
$$-0.06328\mathcal{M}_3 + 0.12041\mathcal{M}_4 + 0.12041\mathcal{M}_5, \tag{5.4}$$

$$\mathcal{M}_2/\mathcal{A}_2 = +9.2950 \times 10^9 + 0.05918\mathcal{M}_1 + 0.05918\mathcal{M}_2$$
$$+0.48414\mathcal{M}_3 - 0.15330\mathcal{M}_4 - 0.15330\mathcal{M}_5, \tag{5.5}$$

$$\mathcal{M}_3/\mathcal{A}_3 = +30.2889 \times 10^9 - 0.06328\mathcal{M}_1 + 0.48414\mathcal{M}_2$$
$$+0.05918\mathcal{M}_3 + 0.12041\mathcal{M}_4 + 0.12041\mathcal{M}_5, \tag{5.6}$$

$$\mathcal{M}_4/\mathcal{A}_4 = -4.6312 \times 10^9 + 0.12041\mathcal{M}_1 - 0.15330\mathcal{M}_2$$
$$+0.12041\mathcal{M}_3 + 0.05918\mathcal{M}_4 - 0.06328\mathcal{M}_5, \tag{5.7}$$

$$\mathcal{M}_5/\mathcal{A}_5 = -4.6312 \times 10^9 + 0.12041\mathcal{M}_1 - 0.15330\mathcal{M}_2$$
$$+0.12041\mathcal{M}_3 - 0.06328\mathcal{M}_4 + 0.05918\mathcal{M}_5. \tag{5.8}$$

The fact that the $O_{b(\mathrm{i})}$ and $O_{b(\mathrm{ii})}$ ions are in the same crystallographic positions means that they have fields of identical magnitude acting on them, and so will have not only identical polarizabilities, but also equal dipole moments. Therefore $\mathcal{A}_5$ and $\mathcal{M}_5$ can be replaced by $\mathcal{A}_4$ and $\mathcal{M}_4$ respectively in the above equations. Nevertheless, the $O_{b(\mathrm{i})}$ and $O_{b(\mathrm{ii})}$ ions occupy separate cubic lattices, and so each array creates a field at its own lattice points which is different from that it creates at the lattice points of the other, as is evident from the last two terms in equations (5.7) and (5.8). Making the suggested simplification, the four resulting equations may now be solved so that the electronic dipole moment of each ion is given in terms of the polarizabilities of all of the ions; thus

$$\mathcal{M}_k = f_k(\mathcal{A}_1, \mathcal{A}_2, \mathcal{A}_3, \mathcal{A}_4). \tag{5.9}$$

Since

$$\mathcal{M}_k = \mathcal{A}_k E_k, \tag{5.10}$$

where $E_k$ is the total electrostatic field at the $k$th ion, it follows that we have directly

$$E_k = (1/\mathcal{A}_k)f_k(\mathcal{A}_1, \mathcal{A}_2, \mathcal{A}_3, \mathcal{A}_4). \tag{5.11}$$

Proceeding in that way, after some algebra we find

$$E_1 = K^{-1}(+3.70510 + 0.33077\mathcal{A}_2 - 2.13596\mathcal{A}_3 - 1.10009\mathcal{A}_4 - 0.19154\mathcal{A}_2\mathcal{A}_3$$
$$-0.36590\mathcal{A}_2\mathcal{A}_4 + 0.89866\mathcal{A}_3\mathcal{A}_4 - 0.09156\mathcal{A}_2\mathcal{A}_3\mathcal{A}_4) \times 10^9, \tag{5.12}$$

$$E_2 = K^{-1}(+9.29500 - 0.33077\mathcal{A}_1 + 14.11419\mathcal{A}_3 + 1.45804\mathcal{A}_4 - 1.11241\mathcal{A}_1\mathcal{A}_3$$
$$-0.55771\mathcal{A}_1\mathcal{A}_4 - 1.95382\mathcal{A}_3\mathcal{A}_4 - 0.03896\mathcal{A}_1\mathcal{A}_3\mathcal{A}_4) \times 10^9, \tag{5.13}$$

$$E_3 = K^{-1}(+30.28891 - 2.02697\mathcal{A}_1 + 2.70755\mathcal{A}_2 - 0.99097\mathcal{A}_4 - 0.18109\mathcal{A}_1\mathcal{A}_2$$
$$-0.64258\mathcal{A}_1\mathcal{A}_4 - 1.00222\mathcal{A}_2\mathcal{A}_4 + 0.04353\mathcal{A}_1\mathcal{A}_2\mathcal{A}_4) \times 10^9, \tag{5.14}$$

$$E_4 = K^{-1}(-4.63108 + 0.72019\mathcal{A}_1 - 1.15083\mathcal{A}_2 + 3.92119\mathcal{A}_3 + 0.09054\mathcal{A}_1\mathcal{A}_2$$
$$-0.49893\mathcal{A}_1\mathcal{A}_3 - 0.76836\mathcal{A}_2\mathcal{A}_3 + 0.04353\mathcal{A}_1\mathcal{A}_2\mathcal{A}_3) \times 10^9, \tag{5.15}$$

where

$$K = (+1.00000 - 0.05918\mathcal{A}_1 - 0.05918\mathcal{A}_2 - 0.05918\mathcal{A}_3 + 0.00410\mathcal{A}_4$$
$$-0.00050\mathcal{A}_1\mathcal{A}_3 - 0.02924\mathcal{A}_1\mathcal{A}_4 - 0.23089\mathcal{A}_2\mathcal{A}_3 - 0.04724\mathcal{A}_2\mathcal{A}_4$$
$$-0.02924\mathcal{A}_3\mathcal{A}_4 + 0.01774\mathcal{A}_1\mathcal{A}_2\mathcal{A}_3 + 0.00887\mathcal{A}_1\mathcal{A}_2\mathcal{A}_4$$
$$+0.00710\mathcal{A}_1\mathcal{A}_3\mathcal{A}_4 + 0.03930\mathcal{A}_2\mathcal{A}_3\mathcal{A}_4). \tag{5.16}$$

The field $E_5$ is equal to the field $E_4$.

## 6. Relationship between electronic polarizabilities and electronic polarization

We now wish to derive the contribution $P_{ek}$ to the electronic polarization $P_e$ made by each species of ion. This is related to dipole moment as follows:

$$P_{ek} = \mu_{ek}/a^3. \tag{6.1}$$

On substituting the appropriate value for $a$, this gives

$$P_{ek} = 1.5719 \times 10^{-12}\mathcal{A}_k E_k. \tag{6.2}$$

Substitution of the expressions for $E_k$ given in equations (5.12) to (5.15) into equation (6.2) gives

$$P_{e1} = K^{-1}(+5.82409\mathcal{A}_1 + 0.51994\mathcal{A}_1\mathcal{A}_2 - 3.35754\mathcal{A}_1\mathcal{A}_3 - 1.72925\mathcal{A}_1\mathcal{A}_4$$
$$-0.30108\mathcal{A}_1\mathcal{A}_2\mathcal{A}_3 - 0.57516\mathcal{A}_1\mathcal{A}_2\mathcal{A}_4 + 1.41262\mathcal{A}_1\mathcal{A}_3\mathcal{A}_4$$
$$-0.14392\mathcal{A}_1\mathcal{A}_2\mathcal{A}_3\mathcal{A}_4) \times 10^{-3}, \tag{6.3}$$

$$P_{e2} = K^{-1}(+14.61093\mathcal{A}_2 - 0.51994\mathcal{A}_1\mathcal{A}_2 + 22.18627\mathcal{A}_2\mathcal{A}_3 + 2.29191\mathcal{A}_2\mathcal{A}_4$$
$$-1.74861\mathcal{A}_1\mathcal{A}_2\mathcal{A}_3 - 0.87667\mathcal{A}_1\mathcal{A}_2\mathcal{A}_4 - 3.07123\mathcal{A}_2\mathcal{A}_3\mathcal{A}_4$$
$$-0.06124\mathcal{A}_1\mathcal{A}_2\mathcal{A}_3\mathcal{A}_4) \times 10^{-3}, \tag{6.4}$$

$$P_{e3} = K^{-1}(+47.61152\mathcal{A}_3 - 3.18622\mathcal{A}_1\mathcal{A}_3 + 4.25603\mathcal{A}_2\mathcal{A}_3 - 1.55772\mathcal{A}_3\mathcal{A}_4$$
$$-0.28466\mathcal{A}_1\mathcal{A}_2\mathcal{A}_3 - 1.01008\mathcal{A}_1\mathcal{A}_3\mathcal{A}_4 - 1.57540\mathcal{A}_2\mathcal{A}_3\mathcal{A}_4$$
$$+0.06843\mathcal{A}_1\mathcal{A}_2\mathcal{A}_3\mathcal{A}_4) \times 10^{-3}, \tag{6.5}$$

$$P_{e4} = K^{-1}(-7.27965\mathcal{A}_4 + 1.13208\mathcal{A}_1\mathcal{A}_4 - 1.80900\mathcal{A}_2\mathcal{A}_4 + 6.16377\mathcal{A}_3\mathcal{A}_4$$
$$+0.14232\mathcal{A}_1\mathcal{A}_2\mathcal{A}_4 - 0.78427\mathcal{A}_1\mathcal{A}_3\mathcal{A}_4 - 1.20779\mathcal{A}_2\mathcal{A}_3\mathcal{A}_4$$
$$+0.06843\mathcal{A}_1\mathcal{A}_2\mathcal{A}_3\mathcal{A}_4) \times 10^{-3}. \tag{6.6}$$

These can be summed to find $P_e$, but an additional expression for $P_{e5}$, identical to that for $P_{e4}$, must be added to represent the contribution of the electronic polarization of the $O_{b(ii)}$ ion. When that is done, we arrive at the following expression for

$P_e$:

$$P_e = K^{-1}(+5.82409\mathcal{A}_1 + 14.61093\mathcal{A}_2 + 47.61152\mathcal{A}_3 - 14.55930\mathcal{A}_4$$
$$-6.54376\mathcal{A}_1\mathcal{A}_3 + 0.53491\mathcal{A}_1\mathcal{A}_4 + 26.44230\mathcal{A}_2\mathcal{A}_3 - 1.32609\mathcal{A}_2\mathcal{A}_4$$
$$+10.76982\mathcal{A}_3\mathcal{A}_4 - 2.33435\mathcal{A}_1\mathcal{A}_2\mathcal{A}_3 - 1.16719\mathcal{A}_1\mathcal{A}_2\mathcal{A}_4$$
$$-1.16600\mathcal{A}_1\mathcal{A}_3\mathcal{A}_4 - 7.06221\mathcal{A}_2\mathcal{A}_3\mathcal{A}_4) \times 10^{-3}. \tag{6.7}$$

It will be noticed that not all of the $\mathcal{A}_k$ product terms are present, for example the $\mathcal{A}_1\mathcal{A}_2\mathcal{A}_3\mathcal{A}_4$ term. That is because their coefficients are either negligible or zero.

It was shown in §2 that the polarization $P_q$ caused by the displacement of ionic charges is 0.13164. In order for our model to predict the experimental result of a polarization $P$ of 0.261, it is therefore required that $P_e$ should be 0.12936. If that value is inserted into equation (6.7) then it may be rearranged to give

$$+0.10420\mathcal{A}_1 + 0.17213\mathcal{A}_2 + 0.42723\mathcal{A}_3 - 0.11665\mathcal{A}_4 - 0.05009\mathcal{A}_1\mathcal{A}_3$$
$$+0.03338\mathcal{A}_1\mathcal{A}_4 + 0.43530\mathcal{A}_2\mathcal{A}_3 + 0.03699\mathcal{A}_2\mathcal{A}_4 + 0.11249\mathcal{A}_3\mathcal{A}_4$$
$$-0.03579\mathcal{A}_1\mathcal{A}_2\mathcal{A}_3 - 0.01789\mathcal{A}_1\mathcal{A}_2\mathcal{A}_4 - 0.01611\mathcal{A}_1\mathcal{A}_3\mathcal{A}_4 - 0.09389\mathcal{A}_2\mathcal{A}_3\mathcal{A}_4 = +1. \tag{6.8}$$

If the values of $\mathcal{A}_1$, $\mathcal{A}_2$, $\mathcal{A}_3$, $\mathcal{A}_4$ are such that this equation is satisfied, then the experimental value of $P$ is predicted; thus equation (6.8) stipulates the first condition to be satisfied by the electronic polarizabilities of the ions. It is possible to find reasonable values for these polarizabilities that do satisfy the equation, but there are an indefinitely large number of sets of values which would do so, and the fact that some of them are in accordance with reasonable expectations is hardly a satisfactory check on the predictive powers of the model. In the following section a further constraint is introduced by the derivation of an equation which must be satisfied concerning the relationship of the electronic susceptibility $\chi_e$ and the polarizability factors $\mathcal{A}_k$.

## 7. Relationship between electronic polarizabilities and refractive index

We shall consider a ray of light travelling transversally across the crystal, plane polarized so that its electric field of instantaneous value $E_r$ is in the $z$ direction, i.e. the vertically polarized ray. To be in the visible spectrum, its frequency must be between about $4 \times 10^{14}$ and $8 \times 10^{14}$. The nuclei of the ions are too massive to be affected significantly by an electric field of such a high frequency, but their electron clouds are able to respond to it. The result is that a high frequency polarization of instantaneous value $P_r$ is set up, given by

$$P_r = \epsilon_0 E_r \chi_e, \tag{7.1}$$

where $\chi_e$ is the electronic susceptibility of the material for fields in the $z$ direction.

This susceptibility is linked to the corresponding relative permittivity $\epsilon_r$ of the material at optical frequencies by the relationship

$$\chi_e = \epsilon_r - 1. \tag{7.2}$$

The refractive index relating to the ray of light being considered is usually denoted by the symbol $n_c$. Since the square of the refractive index $n_c$ also gives $\epsilon_r$, we have

$$P_r = \epsilon_0 E_r (n_c^2 - 1). \tag{7.3}$$

The value of the polarization $P_r$ resulting from the response of the electron clouds to an applied field $E_r$ will now be calculated in terms of the polarizability factors $\mathcal{A}_k$. It will then be related to the value of the appropriate refractive index, so that another equation corresponding to equation (6.8) can be formulated which has to be satisfied by $\mathcal{A}_1$, $\mathcal{A}_2$, $\mathcal{A}_3$, $\mathcal{A}_4$.

### ( *a* ) *Derivation of expressions for the fields at ions caused by a high-frequency applied field*

Since the applied field $E_r$ caused by the vertically polarized ray does not change the positions of the ionic charges, it does not change the fields caused by them. Provided that the optical frequency is much less than that of the resonant frequency of the electron cloud, its movement is in phase with $E_r$, and at any instant the field created by the electronic polarization is the same as if the field $E_r$ did not vary with time.

We can therefore find the field at every ion by using equations (5.4) to (5.8) inclusive, but with the term $E_r$ added to the right-hand side of each. The first term on the right-hand side of each is the same, because the ionic displacements are unchanged. The coefficients of the $\mathcal{M}_k$ terms are also unchanged, but the $E_r$ values, and so the $\mathcal{M}_k$ values, are changed by the presence of $E_r$ and by the change in the field at each ion caused by the change in the electronic dipole moments of all the ions.

The new set of five simultaneous equations can be reduced to four by replacing $\mathcal{A}_5$ and $\mathcal{M}_5$ by $\mathcal{A}_4$ and $\mathcal{M}_4$ respectively, and can be solved in the same way as were the first set to give new values of $E_k$ in terms of $\mathcal{A}_1$, $\mathcal{A}_2$, $\mathcal{A}_3$, $\mathcal{A}_4$. The previous expressions for $E_k$, given in equations (5.12)–(5.15) can now be subtracted from the new expressions in order to give expressions in terms of $\mathcal{A}_k$ of the components of the new $E_k$ values which are attributable to the presence of $E_r$. These and related dipole moments and polarizations will be designated by the additional suffix $r$, as a reminder that they are due to the presence of the ray.

Proceeding as described above, after some algebra we have

$$E_{1r} = K^{-1}(+1.00000 - 0.12246\mathcal{A}_3 + 0.24492\mathcal{A}_4 - 0.23263\mathcal{A}_2\mathcal{A}_3$$
$$-0.11632\mathcal{A}_2\mathcal{A}_4 - 0.02999\mathcal{A}_3\mathcal{A}_4)E_r, \tag{7.4}$$

$$E_{2r} = K^{-1}(+1.00000 + 0.42497\mathcal{A}_3 - 0.30250\mathcal{A}_4 - 0.06704\mathcal{A}_1\mathcal{A}_3$$
$$-0.03352\mathcal{A}_1\mathcal{A}_4 + 0.07056\mathcal{A}_3\mathcal{A}_4)E_r, \tag{7.5}$$

$$E_{3r} = K^{-1}(+1.00000 - 0.12246\mathcal{A}_1 + 0.42496\mathcal{A}_2 + 0.24492\mathcal{A}_4$$
$$-0.02999\mathcal{A}_1\mathcal{A}_4 - 0.24486\mathcal{A}_2\mathcal{A}_4)E_r, \tag{7.6}$$

$$E_{4r} = K^{-1}(+1.00000 + 0.06123\mathcal{A}_1 - 0.21248\mathcal{A}_2 + 0.06123\mathcal{A}_3$$
$$-0.02999\mathcal{A}_1\mathcal{A}_3 - 0.24487\mathcal{A}_2\mathcal{A}_3)E_r, \tag{7.7}$$

where $K$ is given by equation (5.16).

The field $E_{5r}$ is equal to the field $E_{4r}$.

### ( *b* ) *Relationship between electronic polarizabilities and electronic susceptibility*

Now applying the relationship of equation (7.1), we have

$$\chi_e = \frac{1}{\epsilon_0 E_r} \sum_1^5 P_{kr} = \frac{1}{\epsilon_0 E_r} \sum_1^5 \frac{\mu_{ekr}}{a^3} = \frac{0.17753}{E_r} \sum_1^5 \mathcal{A}_k E_{kr}. \tag{7.8}$$

Multiplying each equation for $E_{kr}$ by the factor $\mathcal{A}_k$, and summing the results, including a term identical to that yielded by equation (7.7) to account for the contribution of the $O_{b(ii)}$ ion, from equation (7.8) we obtain

$$
\begin{aligned}
\chi_e = 0.17753 K^{-1}(&\mathcal{A}_1 + \mathcal{A}_2 + \mathcal{A}_3 + 2\mathcal{A}_4 - 0.24492\mathcal{A}_1\mathcal{A}_3 + 0.36738\mathcal{A}_1\mathcal{A}_4 \\
&+ 0.84994\mathcal{A}_2\mathcal{A}_3 - 0.72746\mathcal{A}_2\mathcal{A}_4 + 0.36738\mathcal{A}_3\mathcal{A}_4 - 0.29967\mathcal{A}_1\mathcal{A}_2\mathcal{A}_3 \\
&- 0.14984\mathcal{A}_1\mathcal{A}_2\mathcal{A}_4 - 0.11996\mathcal{A}_1\mathcal{A}_3\mathcal{A}_4 - 0.66402\mathcal{A}_2\mathcal{A}_3\mathcal{A}_4).
\end{aligned}
\tag{7.9}
$$

(*c*) *Derivation of electronic susceptibility from observations of refractive index*

The value of $\chi_e$ to be inserted in equation (7.9) should be derived from experiments to measure the refractive index related to the vertically polarized ray at frequencies so high that the ions are not disturbed, but not so high that observations are in the electronic dipole resonance region. Experimental results were obtained by Johnston (1971) using the vertically polarized ray in single crystals of barium titanate relating to the variation of refractive index for free-space wavelengths $\lambda$ in the range of about 0.46–0.66 µm. Over this range the measured refractive index $n_c$ drops continuously from about 2.49 to about 2.36, the graph having the typical shape of the skirt of a resonance curve.

Because $n_c$ is changing with wavelength, there are some complications. Energy losses are occurring, and the polarization is not in phase with the applied field. It is necessary to establish values for $n_c$ relating to lower frequencies, well clear of the resonance region, and to use the value to which the experimental curve tends as $\lambda$ becomes indefinitely large. This can be done by the analytical extrapolation of the experimental curve in the visible region; it could not be done at very low frequencies by experiment because the electric field of the ray would cause movement of the ions.

When the centroid of a spherical electron cloud of uniform density is separated from that of the nucleus of an atom or ion, its polarizability does not vary with applied field and there is a restoring force created on the separated charges proportional to the displacement $z$. It follows that when a sinusoidal electric field is applied, then except for frequencies very close to resonance, $z$ is given by

$$
z = \frac{\beta}{\omega_0^2 - \omega^2} \sin \omega t,
\tag{7.10}
$$

where $\beta$ is a constant with dimensions m s$^{-2}$, $\omega_0$ is the angular frequency at resonance, and $\omega$ is the angular frequency of the applied field. Therefore the resulting dipole moment and so polarization are given by expressions of the same form, but with different constants. Hence from equation (7.10) we have

$$
\chi_e = \frac{\gamma}{\omega_0^2 - \omega^2},
\tag{7.11}
$$

where $\gamma$ is a constant with dimensions s$^{-2}$. Equation (7.11) may be rewritten

$$
\frac{1}{n_c^2 - 1} = \xi \left[ \frac{1}{\lambda_0^2} - \frac{1}{\lambda^2} \right],
\tag{7.12}
$$

where $\lambda_0$ is the free-space wavelength at angular frequency $\omega_0$, and $\xi$ is a constant with dimensions m$^2$.

Thus if a graph of $1/(n_c^2 - 1)$ against $1/\lambda^2$ is plotted taking values of $n_c$ and $\lambda$ from the experimental curve of Johnston (1971), a straight line is expected. That has been done, and the result is shown in figure 5.
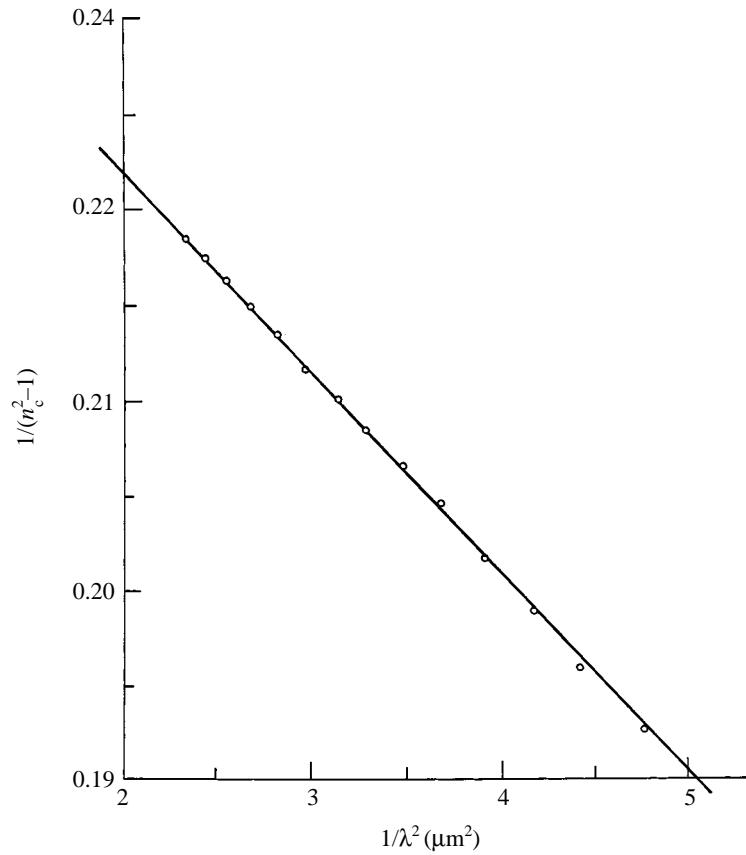
Figure 5. Graph of $1/(n_c^2 - 1)$ against $1/\lambda^2$, where $n_c$ is the refractive index of the vertically polarized ray in BaTiO$_3$, and $\lambda$ is its free-space wavelength in micrometres, derived from the results of Johnston (1971).

The coordinates of the points have been derived by taking $\lambda$ and $n_c$ values from Johnston's curve. It is seen that they do indeed lie on a good straight line. It is well fitted by the equation

$$\frac{1}{n_c^2 - 1} = \frac{1}{1.9}\left[0.4614 - \frac{0.02}{\lambda^2}\right]. \tag{7.13}$$

Here, following Johnston, $\lambda$ is expressed in micrometres.

As $\lambda$ grows indefinitely large, i.e. $\omega$ tends to zero, equation (7.13) gives a value of $n_c$ of 2.2623, and so $\epsilon_r$ and $\chi_e$ have values 5.1179 and 4.1179 respectively. This $\chi_e$ value will be used for equation (7.9).

Equation (7.13) also shows that $\lambda_0$ is 0.2082 μm, corresponding to a frequency of $1.44 \times 10^{15}$. This is in the ultraviolet region, where it would be expected to be. It is possible that due to the spring-like nature of the restoring force, transient radiation of wavelength $\lambda_0$ might be detectable when the crystal structure charges from cubic to tetragonal.

Equation (7.13) can be rewritten to show the direct dependence of $n_c$ on $\lambda$ to give

$$n_c = \left[\frac{118.07\lambda^2 - 1}{23.07\lambda^2 - 1}\right]^{1/2}, \tag{7.14}$$

again with $\lambda$ expressed in micrometres. This equation gives an extremely close fit to Johnston's curve over his entire experimental range.

On insertion of the value of 4.1179 for $\chi_e$ in equation (7.9), it may be rearranged to give

$$+0.10229\mathcal{A}_1 + 0.10229\mathcal{A}_2 + 0.10229\mathcal{A}_3 + 0.08212\mathcal{A}_4 - 0.01006\mathcal{A}_1\mathcal{A}_3$$

$$+0.04508\mathcal{A}_1\mathcal{A}_4 + 0.26753\mathcal{A}_2\mathcal{A}_3 + 0.01588\mathcal{A}_2\mathcal{A}_4 + 0.04508\mathcal{A}_3\mathcal{A}_4 - 0.03066\mathcal{A}_1\mathcal{A}_2\mathcal{A}_3$$

$$-0.01533\mathcal{A}_1\mathcal{A}_2\mathcal{A}_4 - 0.01227\mathcal{A}_1\mathcal{A}_3\mathcal{A}_4 - 0.06793\mathcal{A}_2\mathcal{A}_3\mathcal{A}_4 = +1. \tag{7.15}$$

If the values of $\mathcal{A}_1$, $\mathcal{A}_2$, $\mathcal{A}_3$, $\mathcal{A}_4$ are such that this equation is satisfied, then the value of $\chi_e$ derived from refractive index measurements relating to the vertically polarized ray is predicted. Thus equation (7.15) stipulates the second condition to be satisfied by the electronic polarizabilities of the ions.

### (*d*) *Effect of the finite wavelength of experimental observations*

One further point concerning this calculation should be mentioned. Taking a typical wavelength near the middle of the visible spectrum, say $0.58\,\mu$m, the refractive index for the vertically polarized ray given by Johnston is 2.39. The wavelength of the ray in the crystal is therefore about $0.242\,\mu$m, which is 608 times the length $a$ of the edge of the unit cube. Therefore at a given instant the electric field produced by the ray, although constant along any line in the $z$ direction, changes sign over a distance of about $300a$ in its direction of travel. The Lorentz expression used in the calculation applies for dipoles having the same moment at a given instant over the whole of a cubic lattice of indefinitely large extension in all directions, which implies that the applied field at a given instant should be the same at every lattice point. The question is whether the variation just mentioned casts serious doubts on the validity of the calculation of $\chi_e$.

Such doubts might be assuaged by recalling that the experimental data from the visible spectrum were only used to provide information, by analytical extrapolation, of what data might be expected from notional extremely low frequency measurements carried out with the ions locked in position. At those frequencies, the wavelength would be indefinitely long and the question of the unwelcome variation of fields would therefore not arise. It is true that that variation in field was present during the real experiments in the visible spectrum from which the results of the notional low frequency measurements were deduced. Nevertheless, over the range of the real experiments the wavelength increases by over 40%, and the results as plotted in figure 5 still show the expected straight line, an expectation based only on considerations of resonance. It follows that if an effect caused by field variation is present, then the change to the measured refractive index resulting from it must have such a wavelength dependence that a straight line still results. In that case, the effect of the variation is included in the analytical extrapolation, and will have become negligible at the long wavelength corresponding to the low frequency extrapolated value used for the calculation of $\chi_e$.

## 8. Effect of induced charges on the measuring electrodes

The effect of the application of an externally applied field $E_r$ was analysed in § 7, in the context of the transmission of a vertically polarized ray through the material. There is another way in which an external field can be applied which should now

be considered. The spontaneous polarization is measured by the placing of plane electrodes on the upper and lower surfaces of a specimen of the material in the form of a disc of thickness $t$. These electrodes, in the $xy$ plane, each have a free charge density induced on them by virtue of the spontaneous polarization $P$ of the material, and it is this free charge which is measured to give the value of $P$.

At first sight it might appear that the free charge on the electrodes would give rise to a uniform field $E_f$ in the $+z$ direction in the material, the effect of which would have to be taken into account by the solution of a set of five simultaneous equations, following a procedure similar to that adopted in § 7. In this case, $E_r$ would be replaced by $E_f$, where $E_f$ is given by $P/\epsilon_0$. Furthermore, the ions would be expected to move under the influence of $E_f$, and the consequences of their relative movement would have to be taken into account.

However, further consideration shows that the adoption of the above procedure would be erroneous. It is true that for any $xy$ plane across the material, avoiding the singularities of charges, the integrated value of the $z$ component of electric flux per unit area is $P$, and that this also holds at the planes of the electrodes. However, this flux is not of uniform density, and so neither is the density of the corresponding free charges on the electrodes. Those charges are distributed over the surface in such a way that image charges of the ions of the specimen are set up by the electrodes, which act in the usual manner as mirrors of electric charge.

The consequence is that in an image space of thickness $t$ above and below the electrodes, there are image charges with opposite signs to those in the material. The displacements of these reversed-sign ions is in the opposite direction to those of the real ions, which means that the notional dipoles created by the restoration of the image ionic charges have the same magnitude and direction as those created by the restoration of the real ionic charges. Further consideration shows that the real dipoles caused by electronic polarization also give rise to image dipoles having the same magnitude and direction in the image space as they have in the real material. Because all of the restored ions are in horizontal planes equidistant from each other, the pattern of the positions of the ions, and so the pattern of the positions of the notional and real dipoles associated with them, is identical in the real and image spaces.

The image zones of thickness $t$ adjacent to each electrode are in turn reflected in the electrode further from them, to give second image zones in which the sign of the ionic charges, the directions of their displacements, and the signs and shifts of the electron clouds are the same as those in the real material. In the third image zones, the picture is the same as that in the first image zones. It follows that through an indefinite number of multiple reflections, the notional and real dipole pattern effectively remains the same *ad infinitum* in the positive and negative $z$ directions.

Thus the electrodes, instead of introducing a new complication to be taken into account, in fact effectively extend the material indefinitely in the positive and negative $z$ directions and so help towards the establishment of the conditions necessary for the valid use of the Lorentz formula, which strictly only applies to a system of indefinitely large extension.

There is a caveat that should be mentioned concerning the above argument. In the calculation given in § 2 of the polarization $P_q$ caused by the displacement of ionic charges, the effect of the displacement of each ion was represented by a notional dipole, consequent upon the restoration of the ion to its original lattice point. Because of the crystal symmetry, each restored ion experiences no resultant field from ions of

its own or any other species, and so the ionic charges themselves did not feature in the calculation from then on, but only the notional dipoles to which their displacement gives rise. However, in the system of the real material and its images discussed above, while the charges on ions restored to the lattice points have the same signs in the even numbered image zones as they have in the real material, they have the opposite signs in the odd numbered image zones. Thus it would be not strictly true to say that the restored ions have no influence on each other, or that the electrodes effectively extend the material in exactly the same way as if the real material were to be extended.

However, it is reasonable to suppose that the difference will not be serious. For a typical specimen, say 4 mm thick, there will be about $10^7$ unit cells along a line perpendicular to the electrodes, with a net charge of zero in each unit cell. Both in the real material and in its images, the great majority of the restored ions of a given species will be in an enviroment in which those ions all carry charges of the same sign. It is only very near the electrode surfaces and their images that the difference in the sign of such charges on each side of the boundary might possibly be of some significance notwithstanding the fact that the total charge in each unit cell is still zero on each side of the boundary. Although the ionic charge extension of the material is therefore not quite seamless, the essential fact is that the dipole patterns of both notional dipoles arising from ionic charge displacement, and of real dipoles arising from electron cloud displacement, are continuous indefinitely through the material and its multiple reflections, and it is on those dipole patterns that the analysis is based.

## 9. Calculation of the electronic polarizabilities of ions

The analysis so far has provided two equations, equation (6.8) and equation (7.15), which must be satisfied by the electronic polarizabilities $\alpha_k$ of the ions if experimental observations of spontaneous polarization and refractive index are to be predicted. These constraints are evidently not enough to enable the values of the four unknown quantities, $\mathcal{A}_1$, $\mathcal{A}_2$, $\mathcal{A}_3$, $\mathcal{A}_4$, to be determined.

However, the in-crystal polarizability of barium ions and other constituent ions of ionic solids has been derived by Fowler & Pyper (1985) by a method based on experimental refractive index measurements and the use of a polynomial connecting polarizability and ionic separation, which was taken to be a measure of the environmental constraint on the ion within the crystal. Their best estimate of the polarizability of the barium ion is 10.1 a.u., which is the equivalent in SI units of $1.6653 \times 10^{-40}$ F m$^2$. Although there is a degree of covalent bonding in the BaTiO$_3$ crystal, following Cohen & Krakauer (1990), the barium ion was taken to have its full ionic charge of $+2e$. A value for $\mathcal{A}_1$ of 1.6653 will therefore be adopted in the calculations to follow.

(*a*) *Calculation incorporating an existing value for the polarizability of the* Ba *ion, with the presumption of identical polarizabilities for the* O$_a$ *and* O$_b$ *ions*

Again following Cohen & Krakauer (1990), the present analysis has taken the charge on each oxygen ion to be $-1.63e$. This implies that the O$_a$ and O$_b$ ions each donate an equal charge of $-0.37e$ to the titanium ion, despite their different crystallographic positions. If the polarizabilities of the O$_a$ and O$_b$ ions were also to be independent of crystallographic position, then each could be represented by $\mathcal{A}_3$. Although there is no reason to suppose that the polarizabilities of the O$_a$ and O$_b$

ions are equal, and the implication of their environments is that they probably are not, in order to obtain some rough idea of the fields and forces acting on the ions, the equality of the polarizabilities of the $O_a$ and $O_b$ ions will be provisionally presumed. Thus the polarizability of all of the oxygen ions will be represented by $\mathcal{A}_3$, and since a reliable literature value exists for $\mathcal{A}_1$, the only two unknowns are $\mathcal{A}_2$ and $\mathcal{A}_3$. Their values can therefore be found by the solution of equation (6.8) and equation (7.15).

This calculation takes as its starting point the figure of $1.6653 \times 10^{-40}$ for the in-crystal polarizability of the barium ion (Fowler & Pyper 1985), and takes the polarizability of both kinds of oxygen ion to be the same. The starting point therefore is $\mathcal{A}_1 = 1.6653$ and $\mathcal{A}_4 = \mathcal{A}_3$. Making these substitutions, after some rearrangement equation (6.8) becomes

$$+0.17213\mathcal{A}_2+0.28276\mathcal{A}_3+0.38290\mathcal{A}_2\mathcal{A}_3-0.09389\mathcal{A}_2\mathcal{A}_3^2+0.08566\mathcal{A}_3^2 = 0.82648 \quad (9.1)$$

and equation (7.15) becomes

$$+ 0.10229\mathcal{A}_2 + 0.24273\mathcal{A}_3 + 0.20682\mathcal{A}_2\mathcal{A}_3 - 0.06793\mathcal{A}_2\mathcal{A}_3^2 + 0.02465\mathcal{A}_3^2 = 0.82966. \quad (9.2)$$

Using equation (9.1) and equation (9.2), $\mathcal{A}_2$ may be expressed explicitly in terms of $\mathcal{A}_3$ as follows:

$$\mathcal{A}_2 = \{1.71480\mathcal{A}_3(1 - 0.97838\mathcal{A}_3) - 10.41431\}(1 + 3.15577\mathcal{A}_3)^{-1}. \quad (9.3)$$

Substituting this expression for $\mathcal{A}_2$ into equation (9.1) gives the following equation for $\mathcal{A}_3$:

$$+ \mathcal{A}_3^4 - 3.38432\mathcal{A}_3^3 + 14.75145\mathcal{A}_3^2 - 38.20473\mathcal{A}_3 - 16.62740 = 0. \quad (9.4)$$

This equation for $\mathcal{A}_3$ has four roots, two of them being complex and the other two being real; of the real roots, one is positive and the other negative. Only the positive real root is admissable, giving a value for $\mathcal{A}_3$ of $+3.12336$. Substitution of this value into equation (9.3) gives a value for $\mathcal{A}_2$ of $-1.97347$. Being negative, that is not admissable. The conclusion is that equation (6.8) and equation (7.15), which must be satisfied if the correct values of spontaneous polarization and of refractive index are to be predicted, can not both be satisfied if the polarizability of the Ba ion has the value adopted and if the $O_a$ and $O_b$ ions are postulated to have the same value of polarizability, no matter what is the value of the polarizability of the Ti ion. The present model, incorporating the trustworthy figure for $\mathcal{A}_1$, therefore rules out the possibility of the equality of $\mathcal{A}_3$ and $\mathcal{A}_4$.

### (*b*) *Calculation incorporating existing values for the polarizabilities of the* Ba *ion and the* Ti *ion*

A possibility exists for the evaluation of $\mathcal{A}_3$ and $\mathcal{A}_4$ by making use of a reliably computed value of 1.482 a.u., equivalent to $0.24435 \times 10^{-40}$ F m$^2$, for the polarizability of the titanium ion. This value, due to Johnson *et al.* (1983), is the result of a computation based on a relativistic generalization of the coupled Hartree–Fock theory. The computation relates to an isolated ion having a charge of $+4e$, i.e. possessing 18 electrons, whereas this paper is concerned with an ion in a crystal having a charge of $+2.89e$, i.e. effectively possessing 19.11 electrons; both the magnitude of their charges, and probably more significantly the environment of these ions, are different. Nevertheless, it would be interesting to see what prediction would be made concerning the polarizability of the $O_a$ and $O_b$ ions if the figure of 0.24435 for $\mathcal{A}_2$ were to be adopted. The necessary calculation follows.

Table 7. *The electronic polarizabilities $\alpha_3$ and $\alpha_4$ (F m$^2$) of the oxygen ions $O_a$ and $O_b$ and their ratio, predicted for some presumed values of the electronic polarizability $\alpha_2$ of the titanium ion*

| $\alpha_2 \times 10^{40}$ | 0.2000 | 0.2250 | 0.2443 | 0.2750 | 0.3000 |
|---|---|---|---|---|---|
| $\alpha_3 \times 10^{40}$ | 1.5288 | 1.5185 | 1.5105 | 1.4988 | 1.4882 |
| $\alpha_4 \times 10^{40}$ | 3.5560 | 3.5617 | 3.5666 | 3.5591 | 3.5796 |
| $\alpha_4/\alpha_3$ | 2.3260 | 2.3455 | 2.3612 | 2.3747 | 2.4053 |

The starting point for this calculation therefore is $\mathcal{A}_1 = 1.6653$ and $\mathcal{A}_2 = 0.24435$. Making these substitutions, after some rearrangement equation (6.8) becomes

$$0.43563\mathcal{A}_3 - 0.05930\mathcal{A}_4 + 0.06272\mathcal{A}_3\mathcal{A}_4 = 0.78441 \tag{9.5}$$

and equation (7.15) becomes

$$0.13843\mathcal{A}_3 + 0.15483\mathcal{A}_4 + 0.00805\mathcal{A}_3\mathcal{A}_4 = 0.80467. \tag{9.6}$$

Using equation (9.5) and equation (9.6), $\mathcal{A}_4$ may be expressed explicitly in terms of $\mathcal{A}_3$ as follows:

$$\mathcal{A}_4 = 4.33397 - 0.50805\mathcal{A}_3. \tag{9.7}$$

Substituting this expression for $\mathcal{A}_4$ into equation (9.5) gives the following equation for $\mathcal{A}_3$:

$$\mathcal{A}_3^2 - 23.14722\mathcal{A}_3 + 32.68217 = 0. \tag{9.8}$$

The roots of this equation are $+21.63672$ and $+1.51050$. When these values for $\mathcal{A}_3$ are substituted into equation (9.7) the values for $\mathcal{A}_4$ are given as $-6.65857$ and $+3.56656$ respectively. Since the negative value for $\mathcal{A}_4$ is not admissable, the only acceptable solution is

$$\mathcal{A}_3 = 1.5105, \qquad \mathcal{A}_4 = 3.5666.$$

This gives the ratio of the polarizability of the $O_b$ ion to that of the $O_a$ ion as being 2.3612.

Since there is some doubt about the validity, for the purposes of that calculation, of the value used for the polarizability of the titanium ion, it would be well to assess the sensitivity of the values obtained for $\mathcal{A}_3$ and $\mathcal{A}_4$ to that used for $\mathcal{A}_2$. The calculation above was therefore repeated for some other values of $\mathcal{A}_2$ over the range 0.2–0.3; this range extends over about $\pm 20\%$ of the $\mathcal{A}_2$ value of 0.24435 already adopted.

The admissable results are shown in table 7. When the value adopted for $\mathcal{A}_2$ is reduced by about 18% to 0.2, the $\mathcal{A}_3$ value rises by about 1.2%, the $\mathcal{A}_4$ value falls by about 0.3%, and the $\mathcal{A}_4/\mathcal{A}_3$ ratio falls by about 1.5%. When the adopted $\mathcal{A}_2$ value is increased by about 23% to 0.3, the $\mathcal{A}_3$ value falls by about 1.5%, the $\mathcal{A}_4$ value rises by about 0.36%, and the $\mathcal{A}_4/\mathcal{A}_3$ ratio rises by about 1.9%. The changes in $\mathcal{A}_3$ and $\mathcal{A}_4$ are seen to be quite small compared to the changes in $\mathcal{A}_2$, the variation being not far from linear over the range considered. Throughout that range the variation in the predicted values of $\mathcal{A}_3$ and $\mathcal{A}_4$ from their values resulting from the adopted value for $\mathcal{A}_2$ are not significant, and $\mathcal{A}_4$ remains between about 2.3 and 2.4 times larger than $\mathcal{A}_3$. It therefore seems that even if the true figure for the polarizability of the titanium ion in the crystal were not to agree very closely with the adopted figure,

the results obtained for the in-crystal polarizabilities of the oxygen ions would not be seriously affected.

However, it is quite possible that the true $\mathcal{A}_2$ value might differ from the adopted value of 0.24435 by significantly more than 20%. The state of the titanium ion in the crystal, taken in this paper to have a charge of $2.89e$, might resemble somewhat that of the free $Ti^{+3}$ ion. Although the polarizability of that ion is not known, it would be expected to be greater than that of the $Ti^{+4}$ ion, perhaps by as much as a factor of three. It is therefore worthwhile to calculate how such a large departure from the adopted value would affect the predicted polarizabilities of the $O_a$ and $O_b$ ions.

That calculation has been carried out, with the $\mathcal{A}_1$ value taken to be 1.6653 as before, but with the $\mathcal{A}_2$ value increased by just over a factor of three to 0.7500. The results for $\mathcal{A}_3$ and $\mathcal{A}_4$ are 1.3240 and 3.6874 respectively. Compared with their value when $\mathcal{A}_2$ was taken to be 0.2443, $\mathcal{A}_3$ is 12.34% lower and $\mathcal{A}_4$ is 3.39% higher. These changes, while not negligible, are very much less than the threefold increase in $\mathcal{A}_2$ necessary to bring them about. This means that for the adoption of any reasonable polarizability within a wide range of values for the titanium ion, the predicted values for the polarizabilities of the $O_a$ and $O_b$ ions, particularly the latter, are confined within relatively narrow bounds.

## 10. Specification of the crystal

Taking the literature figures for the electronic polarizabilities of the barium and titanium ions adopted in §9 $b$, and the calculated values for the polarizabilities of the two species of oxygen ion which follow from them, we have a set of $\mathcal{A}_k$ values which satisfy equation (6.8) and equation (7.15), so ensuring that the experimental values of spontaneous polarization and refractive index are predicted by the model. The set of $\mathcal{A}_k$ values are:

$$\mathcal{A}_1 = 1.6653, \quad \mathcal{A}_2 = 0.2444, \quad \mathcal{A}_3 = 1.5105, \quad \mathcal{A}_4 = \mathcal{A}_5 = 3.5666.$$

Having adopted the electronic polarizability values above, it is now possible to draw up a table showing the quantities dealt with in this paper pertaining to the single crystal of barium titanate. These appear in table 8, SI units being used throughout. All figures relate to the model, and so are given to four places of decimals; when these are translated to the real crystal, in general no more than three significant figures are justified. Occasionally, a total may differ in its last figure from the sum of its components because more decimal places were carried than are shown. An explanation follows of how the table was drawn up, with some comments; the numbers in the text correspond to those of the rows in the table.

1. Ionic charge values $q_k$ taking account of electron sharing between the titanium and oxygen ions (see §1).

2. Ionic charge displacements $\Delta z_k$ from the cubic lattice positions when the crystal becomes tetragonal. These displacements are relative to the position of the barium ion, and so only their differences have meaning (see §2).

3. These figures for $\mu_{qk}$, the product of those in rows 1 and 2, have no individual significance, but their sum has, and it gives $\mu_q$, the dipole moment per unit cell due to the relative positions of the charges of its constituent ions. That sum, $8.3741 \times 10^{-30}$, when divided by the volume of the cell, gives the ionic charge polarization $P_q$ to be of value 0.1316 (see §2).

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Table 8. *Results* (SI units) *of the analysis of the electrostatic model for a single crystal of barium titanate*

| | quantity | $j$th ion | Ba | Ti | $O_a$ | $O_{b(i)}$ | $O_{b(ii)}$ |
|---|---|---|---|---|---|---|---|
| | | | $k$th ion | | | | |
| 1 | $q_k \times 10^{19}$ | | +3.2044 | +4.6304 | −2.6116 | −2.6116 | −2.6116 |
| 2 | $\Delta z_k \times 10^{10}$ | | 0 | +0.0544 | −0.1008 | −0.0617 | −0.0617 |
| 3 | $\mu_{qk} \times 10^{30}$ | | 0 | +2.5189 | +2.6325 | +1.6114 | +1.6114 |
| 4 | $E_{qk} \times 10^{-9}$ | | +3.7051 | +9.2950 | +30.2889 | −4.6312 | −4.6312 |
| 5 | $\alpha_k \times 10^{40}$ | | +1.6653 | +0.2444 | +1.5105 | +3.5666 | +3.5666 |
| 6 | $E_k \times 10^{-9}$ | | +1.9636 | +37.1058 | +39.2623 | +1.4921 | +1.4921 |
| 7 | $E_{ek} \times 10^{-9}$ | | −1.7415 | +27.8108 | +8.9734 | +6.1233 | +6.1233 |
| 8 | $\mu_{ek} \times 10^{30}$ | | +0.3270 | +0.9067 | +5.9306 | +0.5322 | +0.5322 |
| 9 | $E_{ejk} \times 10^{-9}$ | Ba | +0.1935 | +0.1935 | −0.2069 | +0.3937 | +0.3937 |
| | | Ti | +0.5366 | +0.5366 | +4.3896 | −1.3900 | −1.3900 |
| | | $O_a$ | −3.7529 | +28.7121 | +3.5096 | +7.1408 | +7.1408 |
| | | $O_{b(i)}$ | +0.6408 | −0.8158 | +0.6408 | +0.3149 | −0.3368 |
| | | $O_{b(ii)}$ | +0.6408 | −0.8158 | +0.6408 | −0.3368 | +0.3149 |
| 10 | $E_{ek} \times 10^{-9}$ | | −1.7413 | +27.8105 | +8.9738 | +6.1228 | +6.1228 |
| 11 | $C_{ejk}$ | Ba | 0 | −0.9189 | +23.2537 | +2.9969 | +2.9969 |
| | | Ti | +0.4789 | 0 | +12.5973 | +2.0406 | +2.0406 |
| | | $O_a$ | +1.0449 | +1.0862 | 0 | +0.9103 | +0.9103 |
| | | $O_{b(i)}$ | +1.5008 | +1.9610 | −10.1444 | 0 | 0 |
| | | $O_{b(ii)}$ | +1.5008 | +1.9610 | −10.1444 | 0 | 0 |
| 12 | $E_{cejk} \times 10^{-9}$ | Ba | 0 | −0.1778 | −4.8117 | +1.1799 | +1.1799 |
| | | Ti | +0.2569 | 0 | +55.2965 | −2.8364 | −2.8364 |
| | | $O_a$ | −3.9216 | +31.1879 | 0 | +6.5001 | +6.5001 |
| | | $O_{b(i)}$ | +0.9617 | −1.5998 | −6.5001 | 0 | 0 |
| | | $O_{b(ii)}$ | +0.9617 | −1.5998 | −6.5001 | 0 | 0 |
| 13 | $E_{cek} \times 10^{-9}$ | | −1.7413 | +27.8106 | +37.4847 | +4.8436 | +4.8436 |
| 14 | $F_{ejk} \times 10^{9}$ | Ba | 0 | −0.0823 | +1.2566 | −0.3082 | −0.3082 |
| | | Ti | +0.0823 | 0 | −14.4413 | +0.7408 | +0.7408 |
| | | $O_a$ | −1.2566 | +14.4413 | 0 | −1.6976 | −1.6976 |
| | | $O_{b(i)}$ | +0.3082 | −0.7408 | +1.6976 | 0 | 0 |
| | | $O_{b(ii)}$ | +0.3082 | −0.7408 | +1.6976 | 0 | 0 |
| 15 | $F_{ek} \times 10^{9}$ | | −0.5579 | +12.8774 | −9.7895 | −1.2650 | −1.2650 |
| 16 | $F_{qk} \times 10^{9}$ | | +1.1873 | +4.3039 | −7.9102 | +1.2095 | +1.2095 |
| 17 | $F_k \times 10^{9}$ | | +0.6294 | +17.1813 | −17.6997 | −0.0555 | −0.0555 |

4. The field $E_{qk}$ at each ionic charge caused by ionic charge displacements, having the $E_{qjk}$ components shown in table 4a (see §3).

5. The set of electronic polarizabilities $\alpha_k$ of the ions (see §9) which gives the required predictions of 0.1294 for electronic polarization $P_e$ and of 4.1179 for the

low frequency electronic susceptibility $\chi_{\mathrm{e}}$ for fields in the $z$ direction (see §6 and §7 respectively).

6. The total electric field $E_k$ at each ion, found by substitution of the values of row 5 in equations (5.12) to (5.16).

7. The field $E_{\mathrm{e}k}$ at each ion caused by all the electronic dipoles, found by subtraction of the figures of row 4 from those of row 6.

8. The electronic dipole moment $\mu_{\mathrm{e}k}$ of each ion, given by the product of the figures of rows 5 and 6. These sum to give an electronic dipole moment per unit cell of $8.2287 \times 10^{-30}$, corresponding to an electronic polarization $P_{\mathrm{e}}$ of 0.1294.

9. The fields $E_{\mathrm{e}jk}$ at the $k$th ions caused by the electronic dipoles of the $j$th ions, calculated by the use of the generalized Lorentz expression of equation (3.1) with tables 2 and 3.

10. The total field $E_{\mathrm{e}k}$ at the $k$th ions caused by the electronic dipoles of all the ions, obtained by the additions of the columns of rows 9; these figures should agree with those of row 7, and they do so to at least four significant figures.

11. The compensation factors $C_{\mathrm{e}jk}$ derived from equation (4.8), from which it is evident that $(C_{\mathrm{e}jk} - 1)(C_{\mathrm{e}kj} - 1) = 1$. This relationship is satisfied within rounding errors by the figures given.

12. The values for $E_{cejk}$, the notional force-field caused by the electronic dipoles of the $j$th ions at each $k$th ion, given by the product of the corresponding figures of rows 9 and 11.

13. The total notional force-field $E_{cek}$ caused by the electronic dipoles of all ions at each $k$th ion, obtained by the summation of the components $E_{cejk}$ of the notional force-fields shown in the columns of rows 12.

14. The electrostatic force $F_{\mathrm{e}jk}$ on each $k$th ion is the sum of the forces caused by the electronic dipole field $E_{\mathrm{e}jk}$ of the dipoles of all of the $j$th ions acting on $q_k$ and the force caused by all of the charges $q_j$ of the $j$th ions acting on the dipole $\mu_{\mathrm{e}k}$ of the $k$th ion. $F_{\mathrm{e}jk}$ is given by the product of the corresponding figures of rows 1 and 12. The diagonal symmetry showing equal and opposite forces illustrates how the compensation factor has ensured that the calculated forces are in accordance with Newton's Third Law.

15. The total electrostatic force $F_{\mathrm{e}k}$ due to the sum of all of the electronic dipole fields acting on the charge $q_k$ of any $k$th ion, and due to all of the ionic charges acting on the electronic dipole $\mu_{\mathrm{e}k}$ of any $k$th ion. $F_{\mathrm{e}k}$ is obtained by the summation of the components $F_{\mathrm{e}jk}$ of the forces shown in the columns of rows 14. The figures in row 15 sum to zero, and so satisfy Newton's Third Law.

16. The electrostatic force $F_{qk}$ on each $k$th ion due to the field caused by ionic charge displacement, given by the products of the figures in rows 1 and 4 (see table 5$a$ for components). The figures in row 16 sum to zero, and so satisfy Newton's Third Law.

17. The total electrostatic force $F_k$ on any $k$th ion, given by the sum of the forces due to the fields arising from ionic charge displacement and from electronic polarization. Again, the figures in this row should and do sum to zero. Since the total force on each ion must be zero, the electrostatic force $F_k$ on each ion must be counterbalanced by an equal and opposite balancing force not derivable independently by means of the model. Since the forces they counterbalance sum to zero in a unit cell, so must the balancing forces.

When tables 4$a$ and 5$a$ supplement table 8 to show the components of $E_{qk}$ and

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Table 9. *The total field $E_{jk}$ (V m$^{-1}$) at each $k$th ion caused by the charges and dipoles of all of the $j$th ions*

(These fields sum to $E_k$ at the $k$th ion.)

| | field $\times 10^{-9}$ $k$th ion | | | | |
|---|---|---|---|---|---|
| $j$th ion | Ba | Ti | $O_a$ | $O_{b(i)}$ | $O_{b(ii)}$ |
| Ba | +0.1935 | −0.8381 | −2.2509 | +2.7743 | +2.7743 |
| Ti | +2.0272 | +0.5366 | +39.1815 | −9.6313 | −9.6313 |
| $O_a$ | −5.4188 | +48.3351 | +3.5096 | +8.3703 | +8.3703 |
| $O_{b(i)}$ | +2.5810 | −5.4640 | −0.5887 | +0.3149 | −0.3368 |
| $O_{b(ii)}$ | +2.5810 | −5.4640 | −0.5887 | −0.3368 | +0.3149 |
| total | +1.9639 | +37.1056 | +39.2628 | +1.4914 | +1.4914 |

Table 10. *The total force $F_{jk}$ (N) on each $k$th ion caused by the charges and dipoles of all of the $j$th ions*

(These forces sum to $F_k$ on the $k$th ion.)

| | force $\times 10^9$ $k$th ion | | | | |
|---|---|---|---|---|---|
| $j$th ion | Ba | Ti | $O_a$ | $O_{b(i)}$ | $O_{b(ii)}$ |
| Ba | 0 | −0.5600 | +1.7904 | −0.9299 | −0.9299 |
| Ti | +0.5600 | 0 | −23.5275 | +2.8931 | +2.8931 |
| $O_a$ | −1.7904 | +23.5275 | 0 | −2.0187 | −2.0187 |
| $O_{b(i)}$ | +0.9299 | −2.8931 | +2.0187 | 0 | 0 |
| $O_{b(ii)}$ | +0.9299 | −2.8931 | +2.0187 | 0 | 0 |
| total | +0.6294 | +17.1813 | −17.6997 | −0.0555 | −0.0555 |

$F_{qk}$ given in rows 4 and 16 respectively, the calculated data concerning the model are complete. However, it is interesting to be able to see directly the electrostatic effect of all of the ions of a given species on any ion of each species. This has been done for fields and forces in table 9 and table 10 respectively.

The fields at each of the $k$th ions caused by the charges and dipoles of all of the $j$th ions are shown in table 9. These figures are the sum of the $E_{qjk}$ values shown in table 4$a$ and the $E_{ejk}$ values given in rows 9 of table 8. Each column of table 9 sums to give the result within rounding errors for $E_k$ shown in row 6 of table 8.

The sum of the electrostatic forces on the charges and dipoles of any $k$th ion caused by the charges and dipoles of all of the $j$th ions, i.e. the electrostatic force caused to act on any ion by each species of ion, is shown in table 10. These figures are the sum of the $F_{qjk}$ values shown in table 5$a$ and the $F_{ejk}$ values given in rows 14 of table 8. Each column of table 10 sums to give the result for $F_k$ shown in row 17 of table 8.

## 11. Conclusions

### (*a*) *Limitations of the model*

The ions of the crystal are represented in the model by arrays of point charges carrying point dipoles. They occupy a vanishingly small volume, whereas the ions have very significant volumes. It is at once evident that the model can tell us nothing directly about the interior of the real ions. However, if their time-averaged charge distribution is such that each ion sets up outside its own volume a quasi-steady field the same as that which would be set up if its own charges were replaced by an appropriate point-charge/point-dipole placed at the position of its nucleus, then the model can simulate the fields set up by the ions outside themselves, i.e. roughly, outside the volume bounded by their six nearest neighbours.

Since the point dipoles of the model are postulated to have dipole moments proportional to the field acting on them, the electronic polarizabilities of the ions of the crystal must not vary significantly with field if the simulation is to be satisfactory. If the crystal ions were to be thought of in a classical way, consisting of a positive point charge surrounded by a cloud of negative charge, then elementary electrostatics indicates that for the ion to have a constant electronic polarizability, the charge cloud must exhibit spherical symmetry, with the further requirement that inside the very small sphere with its centre at the centre of the field-displaced charge cloud, and radius equal to its displacement, the charge cloud density must be everywhere the same. The model therefore does imply something about the interior of the real ions, but of course the classical picture can at best bear a very crude relationship to the sophisticated picture drawn in terms of wavefunctions. Nevertheless, there is some correspondence; in some other contexts the spherical term in the potential surrounding an ion has been found to be dominant (Fowler & Madden 1985), leading to the picture of an ion being enclosed in a spherical 'box', as suggested by Fowler & Pyper (1985). More recently Pyper (1995), in presenting improvements relating to models for fully ionic solid oxides which suppose the environmental energy to be generated by a shell of charge, takes the wavefunctions of the individual ions to be spherically symmetrical.

Turning to optical work carried out on single crystals of barium titanate, the results of the experimental work of Johnston (1971) are well fitted by equations based on the classical ionic model described above, which implies that the ions have dipole moments proportional to the fields acting on them. Taking account of the available evidence, it seems reasonable to suppose that modern descriptions of the charge distribution within an ion in terms of wavefunctions have sufficient spherical symmetry for them to predict an ion which carries an induced dipole arising from a polarizability which is not likely to have a significant variation with applied field. It follows that it is reasonable to simulate the field created by an ion of the crystal outside of the volume it occupies by an appropriate point-charge/point-dipole.

However, it must be emphasized that although the point-charge/point-dipole entities of the model are sometimes not explicitly distinguished in the paper from the ions of the crystal, in that case the distinction is always implicit. The model ions simply represent the crystal ions, and the closeness with which some of their attributes are similar determines the validity of the transfer of results pertaining to the ions of the model to the ions of the crystal. In interpreting the results of the analysis of this paper, it should be borne in mind that even if they are correct for the model, they might not be correct for the crystal because of some deficiency in

the representation of the ions of the crystal by the point-charge/point-dipoles of the model, e.g. if the field of the real ions could only be simulated by an appropriate multipole. Nevertheless, the indications are that within its limitations, the model has sufficient correspondence with reality to have made its examination worthwhile.

### (*b*) *Approximations made in the analysis*

The Lorentz formula relates to the cubic lattice, but it was nevertheless applied to the tetragonal lattice of barium titanate. This will result in a small error, which a rough estimate indicates will lead to an overestimate of $P_q$, and an underestimate of $P_e$, by about 1% in each case; the application of this correction would make the values of $P_q$ and $P_e$ virtually identical. Estimates have not been made of the errors due to this cause in other calculated quantities, but a slight underestimation of $\mathcal{A}_3$ and a slight overestimation of $\mathcal{A}_4$ might be expected.

For the Lorentz formula to hold, the dipoles should be point dipoles, i.e. their length should be negligible in comparison with the length of the unit cube edge. That will certainly be so for the electronic dipoles, which are extremely short. The length of the notional dipoles depends on which ion is providing the reference frame, but as can be seen from table 1, the longest dipole results when the Ti or the $O_a$ ion provides the reference frame, so that the length of the longest notional dipole is $0.1552 \times 10^{-10}$, which is about 3.9% of the length of the cube edge. That is rather long for a point-dipole, but if the notional dipole were considered to be made up of a series of dipoles of infinitesimal length, to each of which a reasonable value for the $S$ factor could be assigned having regard to its variation with position along the cube edge, then an estimate of the resulting error would be obtained. That has not been done, but if the $S$ value were to drop linearly between the points $E_v$ and $L$ of table 3, the field produced at the fixed ion at $L$ by the notional dipole at $E_v$ would be about 1.7% lower than if the nominal dipole had been of negligible length. That is an exaggerated figure, because the $S$ value is passing through its maximum at the point $E_v$, and so its variation over the half-length of the notional dipole will be much less than if it were dropping linearly with distance. An accurate calculation could only be carried out when the functional variation of $S$ along the cube edge were known, but it is reasonably safe to say that no serious error will be introduced on account of the length of the notional dipole.

Although not strictly speaking an approximation in analysis, any uncertainties in the initial data will be reflected in the results. The calculations are quite sensitive to data concerning the positions of, and charges on, the ions. It has been recently remarked by Pyper (1995) that many solid oxides are fully ionic, having a charge of $-2e$ on the oxygen ions. That observation did not relate to perovskite crystals, but the estimate of the charges on the ions of the barium titanate crystal would not have to be greatly modified for the results of the analysis to be significantly different. It would not be difficult to take account of input data modifications by means of a new calculation following the same procedures as those adopted for the present analysis.

### (*c*) *Results of the analysis*

The complete results of the analysis are shown in table 8 supplemented by tables 4*a* and 5*a*; part of that information is presented in a different way in tables 9 and 10. A discussion of these results related to physical quantities of importance in the description of the crystal now follows.

(i) *Concerning polarization*

The total dipole moment per unit cell $\mu$ is given by the sum of $\mu_q$ and $\mu_e$ as $16.6029 \times 10^{-30}$, and the spontaneous polarization $P$ is given by the sum of $P_q$ and $P_e$ as 0.2610, which is the observed experimental value. This means that $P_q$ is about 0.843% below, and $P_e$ is about 0.843% above, one-half of $P$. If the value of $P_q$ is decreased and that of $P_e$ increased for any reason by about 1%, e.g. for the reason given in §11 $b$, then their values become in practice indistinguishable. Thus the spontaneous polarization is due virtually in equal measure to ionic and electronic polarization.

Because of the notional nature of the $\mu_{qk}$ values of row 3 of table 8, it is not possible to break down their sum $\mu_q$ into components attributable to particular species of ion; $\mu_q$, and so $P_q$, are properties of the unit cell. However, the $\mu_{ek}$ values of row 8 of table 8 are real ionic quantities, and from them we can see the relative contributions made to $\mu_e$, and so to $P_e$, by the electronic dipole moment $\mu_{ek}$ of each ion. By far the greatest contribution is made by the $O_a$ ion; about 72% of $\mu_e$ is due to $\mu_{e3}$. The next largest contribution is made by the Ti ion; about 11% of $\mu_e$ is due to $\mu_{e2}$. Those figures show the important part played by the electronic dipole moment of the $O_a$ ion, which is responsible for about 72% of the electronic polarization $P_e$, i.e. about 36% of the total spontaneous polarization $P$.

(ii) *Concerning fields*

The fields $E_{qjk}$ caused at the $k$th ions by the charges of all of the $j$th ions are shown in table 4$a$. The largest is the field caused at the $O_a$ ions by the charges of the Ti ions, greater by a factor of 1.77 than the next largest, the field caused at the Ti ions by the charges of the $O_a$ ions. When all the fields at each $k$th ion caused by the charges of all other ions are added to give $E_{qk}$, the field at the $O_a$ ions is the largest, greater by a factor of 3.26 than the next largest, the field at the Ti ions. The zeros indicate that the charges of any given species of ion can not create a field at their own lattice points. This matter was discussed in §3 $b$.

The fields $E_{ejk}$ caused at each $k$th ion by the electronic dipoles of all of the $j$th ions are shown in rows 9 of table 8. By far the largest is the field caused at the Ti ions by the electronic dipoles of the $O_a$ ions, greater by a factor of 4.02 than the next largest, the field caused at the $O_b$ ions by the electronic dipoles of the $O_a$ ions. When all the fields at any $k$th ion caused by the electronic dipoles of all other ions are added to give $E_{ek}$ as shown in row 10 of table 8, the field at the Ti ions is the largest, greater by a factor of 3.10 than the next largest, the field at the $O_a$ ions. In contrast to the charges, the dipoles of any given species of ion do create a field at their own lattice points, in accordance with the Lorentz formula.

When the fields $E_{qjk}$ and $E_{ejk}$ are added to give the total field $E_{jk}$ at each of the $k$th ions caused by the charges and electronic dipoles of all of the $j$th ions, the results are as shown in table 9. The largest is the field caused at the Ti ions by the $O_a$ ions, greater by a factor of 1.23 than the next largest, the field caused at the $O_a$ ions by the Ti ions. When all the fields at any $k$th ion caused by the charges and electronic dipoles of all other ions are added to give $E_k$, the field at the $O_a$ ion is the largest, but only greater by a factor of 1.06 than the next largest, the field at the Ti ion. The total field at each Ti ion is reduced below that at each $O_a$ ion because the negative field caused by the $O_b$ ions is 9.28 times greater at the Ti ions than it is at the $O_a$ ions. The $E_k$ fields at the Ba and $O_b$ ions are relatively small (see row 6 of table 8).

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That is because for both of these ions, the $E_{qk}$ and $E_{ek}$ fields are in opposition to
each other (see rows 4 and 10 of table 8).

(iii) *Concerning forces*

The forces $F_{qjk}$ on the charge of each $k$th ion caused by the fields $E_{qjk}$ of the
charges of all of the $j$th ions are shown in table 5a. Newton's Third Law leads to
the expectation that $F_{qjk}$ and $F_{qkj}$ should be equal and opposite. That expectation
is fulfilled, as is evident from the figures shown in table 5a. Those figures were each
given independently by the product $q_k E_{qjk}$ with terms taken from row 1 of table 8
and from table 4a respectively, and not obtained by the use of Newton's Law, which
therefore serves as a check on the accuracy of the calculations. It was the failure
to comply with that law which led in §3c to the rejection of table 5b based on the
conventional assumption that the barium ion was undisplaced, and the consequent
derivation in §4a of a compensation factor which was applied in §4b to the figures
of table 5b which turned them into the figures of table 5a, thus demonstrating that
the fixed-frame of reference calculation becomes valid for force calculations if the
compensation factor is used.

The figures of table 5a show that the largest force $F_{qjk}$ is that on the charge of
each Ti ion caused by the charges of all $O_a$ ions, and vice versa, greater by a factor
of 4.22 than the next largest, the corresponding force relating to the Ti ions and the
$O_b$ ions. When all of the forces on the charges of any $k$th ion caused by the charges
of all other ions are added to give $F_{qk}$, the largest is the downward force on each $O_a$
ion, greater by a factor of 1.84 than the upward force on each Ti ion.

The force $F_{ejk}$ is given by the sum of the forces caused by the dipole field of all
of the $j$th ions acting on the charge $q_k$ of any $k$th ion, and of the forces caused by
the charge field of all of the $j$th ions acting on the charges of the dipole $\mu_{ek}$ of any
$k$th ion. From the analysis of §4a, we know that $F_{ejk}$ is given by the product of the
ionic charge $q_k$ and the force-field $E_{cejk}$, values for which are given in row 1 and row
12 respectively of table 8; rows 14 contain the resulting $F_{ejk}$ values. Again it is to be
expected that Newton's Third Law will be satisfied, and inspection of the figures in
row 14 of table 8 shows that that is so, and for all values of $j$ and $k$, $F_{ejk}$ and $F_{ekj}$
are equal and opposite. These figures were obtained by purely electrostatic analysis,
and therefore the fact that they are in accordance with Newton's Law provides a
check on their validity.

The figures show that the largest force $F_{ejk}$ is that on the charge and dipole of
each Ti ion caused by the charges and dipoles of all of the $O_a$ ions, and vice versa,
greater by a factor of 8.51 than the next largest, the corresponding force relating to
the $O_a$ ions and the $O_b$ ions. When all of the forces on the charges and dipoles of any
$k$th ion caused by the dipoles and charges respectively of all other ions are added to
give $F_{ek}$, the largest is the upward force on each Ti ion, greater by a factor of 1.32
than the downward force on each $O_a$ ion.

When the forces $F_{qjk}$ and $F_{ejk}$ are added to give the total electrostatic force $F_{jk}$
caused by all of the $j$th ions on each $k$th ion, the results are those shown in table 10.
The largest force is that caused by all of the Ti ions on each $O_a$ ion, and vice versa,
greater by a factor of 8.13 than the next largest, the corresponding force relating to
the Ti and $O_b$ ions. When all of the electrostatic forces on any $k$th ion caused by all
other ions are added to give $F_k$, the largest is the downward force on the $O_a$ ions,
only slightly greater by a factor of 1.03 than the upward force on the Ti ions. Of the
upward electrostatic force on the ions of a single unit cell, the force on the Ti ion

accounts for 96.47% and the force on the Ba ion for 3.53%; of the equal downward electrostatic force on the ions of the single unit cell, the force on the $O_a$ ion accounts for 99.38%, and the force on each $O_b$ ion accounts for 0.31%. The forces on the Ba and $O_b$ ions are small because for both of them, $F_{qk}$ and $F_{ek}$, each of which is comparatively small, oppose each other (see table 8, rows 15 and 16).

These detailed results support the commonly held view that the Ti and $O_a$ ions play the prevailing part in the determination of the characteristics of the crystal. The electronic dipole moment $\mu_{e3}$ provides about 72% of the electronic polarization $P_e$, (table 8, row 8), and the fields $E_2$ and $E_3$ and the forces $F_2$ and $F_3$ are much greater than the fields and the forces for other $k$ values (see table 8, rows 8 and 17); the force on each Ti ion caused by all of the $O_a$ ions and vice versa (see table 10) is more than eight times the corresponding forces involving any other two species of ions. This means that there is a strong force of compression between each Ti ion and the $O_a$ ion above it.

Although the electrostatic forces on the ions of the unit cell total to zero, there is an electrostatic force $F_k$ on each ion as given in row 17 of table 8. Since the ions are stationary, they each must be acted on by another force $-F_k$, a balancing force which is not derivable independently by the use of the model. The balancing force is really made up of several component forces, not all of which necessarily are in the opposite direction to the electrostatic forces caused by the charges and dipoles of the ions represented by the model. These components of the balancing force, which have been discussed by Fowler & Pyper (1985) and Pyper (1995), include van der Waals forces, the electrostatic forces caused by the spatial extension of the electron clouds of neighbouring ions, and the force of repulsion arising from the Pauli principle because of the overlap of occupied orbitals (Pyper 1986). These forces are probably in increasing order of magnitude, but the last two have been found to be of about equal importance for anions in some materials (Fowler & Madden 1984, 1985). It is outside the scope of the present model to make predictions about these forces, but it does indicate that they, and any other forces that might be operative, e.g. those due to covalent bonding, should sum to $-F_k$ on the $k$th ion. When the necessary balance of forces can not be maintained, the ions move until they are in new positions where balance is once more possible. That is to say, there is a transition to another structure.

### (iv) *Concerning electronic polarizabilities*

The polarizability of an ion is affected by its environment. It is to be expected that in the confines of a crystal the polarizability of an ion would not be the same as it would be if it were free. While some light cations are very little affected, anions are particularly susceptible to their surroundings (Fowler & Madden 1984, 1985). Those investigators report that the smallest oxide polarizability is $1.87 \times 10^{-40}$ for MgO; all other known values are greater than $2.31 \times 10^{-40}$ (Fowler & Pyper 1985). To turn to compounds having two oxygen ions per formula unit, Fowler *et al.* (1994) have reported polarizabilities for the oxygen ions in the group IV oxides to be in the range $2.45 \times 10^{-40}$ to $2.53 \times 10^{-40}$.

The above polarizability data concerned with formula units having one or two oxygen ions may be compared with the results of the present work, which is concerned with a material having three oxygen ions in its unit cell; values of electronic polarizabilities for the $O_a$ and $O_b$ ions were calculated to be about $1.51 \times 10^{-40}$ and $3.57 \times 10^{-40}$ respectively. At first sight, these values seem somewhat extreme

when compared with those quoted for the polarizability of the oxygen ion in other compounds. However, the total electrostatic force $F_k$ on the $O_a$ ions is 319 times that on the $O_b$ ions (see table 8, row 17), and since the $F_k$ forces are balanced by equal and opposite forces, the compressive force on the $O_a$ ion is so much greater than that on the $O_b$ ion that it is perhaps surprising that the ratio $\alpha_3/\alpha_4$ is not less than 0.424 (see table 8, row 5). An even smaller ratio with correspondingly more extreme values for $\alpha_3$ and $\alpha_4$ would not have seemed amiss. Furthermore, *ab initio* calculations of anion polarizabilities show that they vary strongly from one crystal to another (Fowler & Pyper 1985).

In that same paper, the in-crystal polarizability of the Ba ion was estimated to be 10.1 a.u. (i.e. $1.665 \times 10^{-40}$ F m$^2$), a figure which has been adopted here for the calculations appearing in §9. In addition, the authors give in their table 1 figures derived for the total polarizabilities per formula unit relating to a range of ionic compounds. These include BaO, for which the value shown is 4.6683 Å$^3$ (i.e. $5.194 \times 10^{-40}$ F m$^2$). Subtracting the barium ion polarizability from this yields an oxygen ion polarizability of about $3.53 \times 10^{-40}$ F m$^2$. That figure is only about 1% below the figure of $3.57 \times 10^{-40}$ F m$^2$ derived in this paper for the $O_b$ ions in BaTiO$_3$. This agreement gives some reassurance that calculated values of oxide polarizabilities may fall outside the usual range and yet be well grounded. Fowler *et al.* (1994) have found that the polarizabilities of the oxygen ions in the group IV dioxides depend on the closest cation–anion separation, as is the case for the alkali oxides, which have only one oxygen ion; it may well be that the same separation plays a significant part in determining the polarizabilities of the $O_a$ and $O_b$ ions in BaTiO$_3$. The calculated values given above therefore seem to be not unreasonable.

### (*d*) *Interfaces*

The electrical characteristics of crystals can be investigated by the use of two kinds of model. The first kind employs wavefunction descriptions of the ions, and involves the techniques of quantum chemistry, including relativistic treatments; sometimes they also draw upon experimental measurements of refractive index. Such treatments can yield results for the polarizabilities of ions within the crystal, and can predict some of the forces between ions, predominantly, but not exclusively, those of a short-range nature.

The second kind of model is of the type analysed in this paper, in which each ion is represented by a point-charge/point-dipole, and the analysis uses only the methods of classical electrostatics to predict the polarizabilities of some ions on the basis of the known polarizabilities of some others, and on the results of laboratory observations of spontaneous polarization and refractive index. This model can also predict the electrostatic forces on each ion, which when added to the forces predicted by the first model, should give the result of zero because each of the ions is in equilibrium. Thus the calculation of balancing forces by means of the two different models gives the first interface between them.

Further, it is reasonable to hope that each model should be capable ultimately of yielding a prediction of the in-crystal polarizability of each ion. That would only be possible for the second model if at least two further experimentally measurable properties of the crystal could be expressed functionally in terms of the electronic polarizabilities of the ions. Then a procedure could be adopted, similar to that already described in relation to spontaneous polarization and refractive index, resulting in additional equations to be satisfied by the electronic polarizabilities of the ions. So far

the only in-crystal polarizability relating to the ions of the $BaTiO_3$ crystal yielded by the first type of model is that for the Ba ion (Fowler & Pyper 1985), already adopted for this paper. Thus the calculation of electronic polarizabilities provides the second interface between the models.

It is evidently not possible to obtain a complete electrical description of the crystal by the use of either the wavefunction model or the point-charge/point-dipole model alone. They describe different aspects of reality each within the boundaries of its own potentialities, and if they were to be developed until their predictions could be brought together so as to fit without dislocation at the interfaces, then we should have a theory of the crystal.

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