

Theory of the Electronic Susceptibilities of Stoichiometric Rutile (TiO_2)

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A theoretical analysis of the symmetry properties of crystalline rutile is made, leading to the conclusion that the isotropic solution of the local field equations for this material is correct. It is shown that this conclusion is supported by the experimentally determined isotropic nature of the magnetic susceptibility of rutile. The isotropic solution of the local field equations yields a value for the electronic polarizability of the titanium ion in rutile of $\alpha_T = 2.2 \text{ \AA}^3$, an order of magnitude greater than the free-ion values usually assigned to the Ti^{4+} ion. This result is supported by a correlation of the ionic sizes as obtained from an electron-density map of rutile determined by x-ray analysis with the polarizabilities in a manner described previously. In addition, this conclusion is in reasonably good quantitative agreement with a theoretical prediction made previously of the effect of the crystalline potential on the cation polarizability. The results of this study give a specific example of a conclusion arrived at in an earlier work to the effect that a cation polarizability in a crystal may be many times its free-ion value. Moreover, it demonstrates the unreliability of the usually accepted additivity rule for the ionic radii.

I. INTRODUCTION

RUTILE is a crystalline material whose unusual properties have attracted the attention of numerous investigators. Although the large body of information available regarding this substance facilitates its theoretical study, it would appear, at least at first glance, that its strongly anisotropic properties would make such a study extremely difficult. However, it will be shown in this work that this very anisotropic nature of rutile can be utilized in reaching certain conclusions regarding its properties which have much wider significance with regard to other crystalline materials.

In a previous study,¹ the electronic polarizabilities of ionic crystals were analyzed by means of the product approximation, which distinguishes groups of electrons in the crystal, but allows for their overlap and mutual interaction. From this procedure, relations were derived which yielded numerical values for the polarizabilities of the ionic constituents of the alkali halide crystals in good agreement with experimentally determined values. Moreover, the results of this study indicated that large fluctuations in the polarizabilities of ions can occur when they are placed in different crystalline environments.

In this work, which in many ways is an extension of the previous study from a somewhat different point of view, the rutile crystal will be analyzed within the approximate framework used previously. In particular, it will be viewed as an ionic crystal, and its properties studied by means of a single configuration generalized antisymmetric product wave function. A theoretical study of the directional properties of ionic constituents in crystals will be applied to an analysis of the observed directional properties of the magnetic susceptibility of rutile. This information added to that obtainable from the anisotropic optical properties of this material will enable an assignment of values to the polarizabilities of the constituent ions. The results achieved in this manner will be shown to confirm the conclusions reached earlier

in that the value of the polarizability of the Ti^{4+} ion in rutile is found to be an order of magnitude greater than the value usually assigned. Moreover, this conclusion is substantiated by an analysis of the extension of the ions in a manner discussed previously in I. It is hoped that this work will prove valuable not only with regard to its conclusion, which departs greatly from the usually held notions having to do with ions in crystals, but also with regard to the method of analysis, which is applicable to the study of other crystalline materials as well.

II. ANALYSIS OF THE MAGNETIC PROPERTIES OF IONIC CRYSTALS WITH APPLICATION TO RUTILE

General Analysis

In general, the contributions to the magnetic susceptibility of a crystalline system which does not undergo a ferro- or antiferromagnetic transition may be grouped into three categories. The first contribution is paramagnetic and obeys the Curie law ($\propto 1/T$) temperature dependence. This contribution arises from the permanent magnetic moments resulting from the spatial and/or spin degeneracy of the ground state and low-lying excited states (states energetically separated from the ground state by an amount comparable to kT) or, more generally, from the statistical average of the mean square moments of the ground and low-lying excited states. The second contribution is also paramagnetic, but not temperature dependent, and is a second-order effect resulting from the induced magnetic polarization of the ground state by the external magnetic field. The diamagnetic contribution falls into the third and final category.²

The ionic crystals of the type under consideration here do not exhibit the Curie-law paramagnetism because their electronic ground states are nondegenerate and energetically separated from the lowest lying ex-

¹ A. R. Ruffa, Phys. Rev. **130**, 1412 (1963). In the following discussion, this work will be referred to as I.

² See, for example, J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932) for a detailed discussion.

cited states by an amount of the order of several electron volts. Parenthetically, then, it may be seen that the temperature at which such a crystalline material begins to display a magnetic susceptibility component that increases with decreasing temperature is a measure of the concentration of impurity ions in the crystal having permanent magnetic moments.³ It is apparent, then, that the magnetic susceptibility of the intrinsic ionic crystal is independent of temperature and has a sign dependent upon whether the paramagnetic or diamagnetic contribution is greater in magnitude. At this point, it is necessary to examine these two contributions in greater detail in order to gain some insight into their analytic behavior.

The paramagnetic contribution is obtained from second-order perturbation theory and, if the magnetic field is in the z direction, is given by²

$$\chi_{\text{para}} = (e^2/2m^2c^2) \sum_{\gamma' \neq \gamma} |\langle \gamma | \mathbf{L}_z | \gamma' \rangle|^2 / E_{\gamma' \gamma}, \quad (1)$$

where $E_{\gamma' \gamma} = E_{\gamma'} - E_{\gamma}$ and

$$\mathbf{L}_z = \sum_{i=1}^N L_{z_i};$$

L_{z_i} is the z component of the orbital angular momentum operator for the i th electron and N is the number of electrons.⁴ This expression is similar to that for the electronic polarizability discussed in I, and may be analyzed in a similar fashion. Expression (1) may be rewritten

$$\chi_{\text{para}} = (e^2/2m^2c^2)(1/\bar{E}_M) \sum_{\gamma' \neq \gamma} |\langle \gamma | \mathbf{L}_z | \gamma' \rangle|^2, \quad (2)$$

where the quantity \bar{E}_M is a magnetic mean excitation energy which is to be distinguished from those discussed in I associated with the electronic polarizability. Applying the principle of spectroscopic stability⁵ in the same manner as in I, one may note that

$$\sum_{\gamma' \neq \gamma} |\langle \gamma | \mathbf{L}_z | \gamma' \rangle|^2 = \sum_{\gamma' \neq \gamma} |\langle \gamma | \mathbf{L}_x | \gamma' \rangle|^2 = \sum_{\gamma' \neq \gamma} |\langle \gamma | \mathbf{L}_y | \gamma' \rangle|^2.$$

³ From a localistic point of view, the wave function of a close-shell ion cannot be induced to acquire any spatial degeneracy by a crystalline potential, regardless of its degree of symmetry, for the following reason. The crystalline potential acting upon the given ion must have contributions each of which transform according to the irreducible representations of the point group of the lattice points surrounding the ion. The resulting perturbed ionic wave function, however, will only have, to first order, a contribution which transforms according to the identity representation, which is one dimensional. As a result, the perturbed wave function is nondegenerate to first order. If it happens that higher-order degenerate contributions are nonnegligible, then a local Jahn-Teller distortion of the lattice points surrounding the ion in question takes place of a magnitude sufficient to remove the degeneracy.

⁴ There is no spin contribution since the ground state is a singlet state.

⁵ A detailed discussion of the validity of the directional independence arguments used here is given in the Appendix.

Consequently, (2) may be written

$$\chi_{\text{para}} = (e^2/6m^2c^2)(1/\bar{E}_M) \langle \gamma | \mathbf{L}^2 | \gamma \rangle, \quad (3)$$

where advantage has been made of the fact that

$$\langle \gamma | \mathbf{L}_x | \gamma \rangle = \langle \gamma | \mathbf{L}_y | \gamma \rangle = \langle \gamma | \mathbf{L}_z | \gamma \rangle = 0$$

for the nondegenerate ground state,² and where $\mathbf{L}^2 = \mathbf{L}_x^2 + \mathbf{L}_y^2 + \mathbf{L}_z^2$.

In a discussion in I, it was shown that within the framework of the product approximation, the expression

$$\langle \gamma | \mathbf{X}^2 | \gamma \rangle = \sum_{i=1}^M \langle \gamma | X_i^2 | \gamma \rangle,$$

and similar expressions for the y and z coordinates are valid for a material having no net electric dipole moment. Here \mathbf{X} is the sum of the x coordinates of all N electrons of the system, X_i is the sum of the x coordinates of the n_i electrons of the i th ion, and M is the number of lattice points. Similarly, it is shown in the Appendix that, for such a material, the relation

$$\langle \gamma | \mathbf{L}^2 | \gamma \rangle = \sum_{i=1}^M \langle \gamma | \mathbf{L}_i^2 | \gamma \rangle$$

is valid, where

$$\mathbf{L}_i^2 = \mathbf{L}_{i_x}^2 + \mathbf{L}_{i_y}^2 + \mathbf{L}_{i_z}^2,$$

and \mathbf{L}_{i_x} , \mathbf{L}_{i_y} , and \mathbf{L}_{i_z} are the sum of the x , y , and z components, respectively, of the orbital angular momentum operators for the electrons of the i th ion.

Making use of the fact that these materials under consideration are magnetically dilute so that the effective local magnetic field acting upon a given ion is essentially the same as the external applied field, Eq. (3) becomes

$$\chi_{\text{para}} = (e^2/6m^2c^2)(1/\bar{E}_M) \sum_{i=1}^M \langle \gamma | \mathbf{L}_i^2 | \gamma \rangle. \quad (4)$$

In terms of the contributions of the ionic constituents, (4) becomes

$$\chi_{\text{para}} = \sum_{i=1}^M \chi_{i \text{ para}} = (e^2/6m^2c^2) \sum_{i=1}^M \langle \gamma | \mathbf{L}_i^2 | \gamma \rangle / \bar{E}_{M_i}, \quad (5)$$

where, in analogy with the discussion in I,

$$\bar{E}_M = \sum_{i=1}^M \chi_{i \text{ para}} \bar{E}_{M_i} / \sum_{i=1}^M \chi_{i \text{ para}}. \quad (6)$$

Written in the manner of (5), it may be seen that the paramagnetic contribution to the susceptibility arises from the fact that the crystalline interaction makes it impossible to choose spherically symmetric probability amplitudes for the ionic electron groups which would render the $\langle \gamma | \mathbf{L}_i^2 | \gamma \rangle$ equal to zero.

The diamagnetic contribution arises from the term of second order in the magnetic field in the Hamilton, and

if the field is in the z direction, is given by

$$\chi_{\text{dia}} = (e^2/4mc^2) \sum_{j=1}^N \langle \gamma | x_j^2 + y_j^2 | \gamma \rangle, \quad (7)$$

where x_j and y_j are the coordinates of the individual electrons. Making use of the matrix sum rule,

$$\langle \gamma | x_j^2 | \gamma \rangle = \sum_{\gamma' \neq \gamma} |\langle \gamma | x_j | \gamma' \rangle|^2 + |\langle \gamma | x_j | \gamma \rangle|^2. \quad (8)$$

With similar expressions for the y_j and z_j , one may again utilize the principle of spectroscopic stability which indicates that

$$\sum_{\gamma' \neq \gamma} |\langle \gamma | x_j | \gamma' \rangle|^2 = \sum_{\gamma' \neq \gamma} |\langle \gamma | y_j | \gamma' \rangle|^2 = \sum_{\gamma' \neq \gamma} |\langle \gamma | z_j | \gamma' \rangle|^2.$$

It may be seen that expression (7) for the diamagnetic susceptibility then reduces to the directionally invariant one

$$\chi_{\text{dia}} = (e^2/6mc^2) \sum_{j=1}^N \langle \gamma | r_j^2 | \gamma \rangle, \quad (9)$$

where $\langle \gamma | r_j^2 | \gamma \rangle = \langle \gamma | x_j^2 + y_j^2 + z_j^2 | \gamma \rangle$, if the material in question displays no net electric dipole moment, i.e., if

$$\langle \gamma | \mathbf{X} | \gamma \rangle = N \langle \gamma | x_i | \gamma \rangle = 0 = \langle \gamma | \mathbf{Y} | \gamma \rangle = \langle \gamma | \mathbf{Z} | \gamma \rangle.$$

Expression (9) is, of course, directly separable into the sum of the contributions of the ionic constituents by the use of a double sum:

$$\chi_{\text{dia}} = \sum_{i=1}^M \chi_{\text{dia}i} = (e^2/6mc^2) \sum_{i=1}^M \sum_{j=1}^{n_i} \langle \gamma | r_j^2 | \gamma \rangle. \quad (10)$$

It is apparent from the above discussion that both contributions to the magnetic susceptibility are independent of direction if the crystal as a whole possesses inversion symmetry. Consequently, one may conclude that the absence of an electric dipole moment in an ionic crystal is a sufficient condition for the directional invariance of its magnetic susceptibility. As a corollary to this statement, one may infer that, in general, the conditions of internal symmetry of an ionic crystal are usually such that the directional invariance of its magnetic susceptibility is direct evidence of the fact that it does not possess an electric dipole moment.

Application to Rutile

The above discussion of the magnetic properties of ionic crystals may be used in the analysis of the careful measurement of the magnetic susceptibility of rutile made recently by Senftle, Pankey, and Grant.⁶ The temperature independence of the susceptibility above 55°K measured by these workers is an excellent indication of the high purity of the specimens used. Al-

though the increase in the susceptibility at liquid-helium temperature was explained on the basis of the possible existence of Ti^{3+} sites resulting from oxygen loss in too small a concentration to be detectable, the admittedly large experimental error in this region probably was responsible for most of the increase.

The positive sign of the susceptibility found by these investigators indicates the dominance of the paramagnetic term from which one may infer the existence of a large distortion of the ionic probability amplitudes from spherical symmetry. More important from the standpoint of this study, however, is the fact that the susceptibility of single-crystal rutile was found to be independent of the orientation of the crystal axis with respect to the magnetic field. This finding, although surprising to these investigators because of the strongly anisotropic dielectric constant of rutile, is nevertheless a direct indication of the absence of a net electric dipole moment in this material, since its crystal structure does not admit the possibility of nonzero but equal electric dipole moments in the x , y , and z directions. This conclusion is in accord with the fact that rutile is not observed to undergo a ferroelectric transition down to 1.6°K.⁷

III. DETERMINATION OF THE POLARIZABILITIES OF THE IONIC CONSTITUENTS IN RUTILE

By making full use of a detailed analysis of the internal symmetry of crystalline rutile, it is possible, with only the simplest of assumptions and the use of the information discussed above, to arrive at unique values for the electronic polarizabilities of its ionic constituents. The polarizabilities of the oxygen and titanium ions parallel and perpendicular to the c axis constitute the four unknown quantities. The optical birefringence of rutile provides two of the four conditions necessary to obtain unique values for these four unknowns. It is shown below that the other two conditions are given by the effective directional invariance of the electronic polarizabilities of the ions.

In the notation of I, the polarization of the crystalline system is given by

$$\mathbf{P} = (2e^2/\bar{E}_{3s}) \sum_{i=1}^M \mathcal{E}_i \langle \gamma | X_i^2 | \gamma \rangle, \quad (11)$$

where \mathcal{E}_i is the effective local field acting upon the i th ion, and \bar{E}_{3s} is the mean excitation energy of the third kind for the system defined in I. The quantity $\langle \gamma | X_i^2 | \gamma \rangle$ may be set equal to the sum of $|\langle \gamma | X_i | \gamma \rangle|^2$ and the directionally independent quantity

$$\sum_{\gamma' \neq \gamma} |\langle \gamma | X_i | \gamma' \rangle|^2.$$

In a material possessing over-all inversion symmetry, the $\langle \gamma | X_i | \gamma \rangle$ are either all zero, or cancel pairwise. It is

⁶ F. E. Senftle, T. Pankey, and F. A. Grant, Phys. Rev. **120**, 820 (1960).

⁷ R. A. Parker, Phys. Rev. **124**, 1719 (1961).

evident that, in the first case, the ionic polarizabilities are directionally invariant. In the second case, there is an effective directional independence of the ionic polarizabilities if the local fields at the ions having opposite transformation properties under the inversion operation are equal. In this case, the effects of the dipole moments cancel, and the total polarization is the same as if no dipole moments existed, and is equal to the sum of the directionally invariant contributions.

In the case of rutile, the titanium sites are at Wyckoff positions *a* with point symmetry *mmm*. This position has a center of symmetry so that the titanium ions do not acquire an electric dipole moment from the lattice environment. On the other hand, the oxygen ion sites are at Wyckoff positions *f* with point symmetry *mm*, which does not have a center of symmetry. However, these sites can be taken in pairs in which the environment of one is the mirror image of the other.⁸ Consequently, any electric dipole moment acquired by the ions of these pairs as a result of the effect of the lattice environment cancel.

Detailed analyses of the local field at the lattice sites of rutile have been carried out independently and almost simultaneously by Parker⁹ and by Bolton, Fawcett, and Gurney (BFG).¹⁰ In each of these two studies, the local field acting on a given ion was expressed as a sum of the resultant field due to dipoles inside a cavity and a continuum region outside the cavity. In the first study, the dipole sum was calculated by the Ewald-Kornfeld method, which is equivalent to performing a sum inside a spherical cavity of dimension large enough to insure the convergence of the sum. The second study, in contrast, noted that finite sums performed inside spherical cavities do not converge uniformly to a fixed value, but instead oscillate about the point of ultimate convergence. In order to obtain uniform convergence, they chose cavities of successively larger sizes having the shape of the crystalline unit cell. The components of the Lorentz factor were then obtained by extrapolation of these results to a cavity of dimension large enough to insure convergence. It would appear that these two procedures should yield the same results, but as is discussed below, they do not. Since the Ewald-Kornfeld method used by Parker should yield the correct value of convergence of the dipole sum, it is possible that the extrapolation procedure which was used by BFG was not completely accurate.

In both of these studies, the local-field equations were solved by assuming a small value for the titanium ion polarizability, and values for the oxygen ion polarizability in the direction of the *c* axis and in the [110] direction were obtained. Parker chose the Pauling value 0.187 Å³ while BFG chose the value 0.20±05 Å³ for the

titanium ion polarizability. The values which they obtained for the oxygen ion polarizability in the *c* direction for λ=5893 Å are almost identical, but Parker's value is somewhat larger for the value of the polarizability in the [110] direction. It is interesting to note that BFG solve the local-field equations for the isotropic case, i.e., the case in which the oxygen and titanium polarizabilities are independent of direction, but rejected the result because of the large value of the titanium polarizability obtained. The solution for λ=∞ which they obtained was α_T=2.73 Å³ and α₀=0.59 Å³ for the titanium and oxygen ion polarizabilities, respectively. Parker's local-field equations have been solved by the author for the isotropic case¹¹ for λ=∞, and the values α_T=2.20 Å³ and α₀=0.86 Å³ have been obtained. The two sets of results are not as inconsistent as they may appear since small differences in the calculated values of the components of the Lorentz factor can result in relatively large differences in the polarizabilities calculated from the isotropic solution of the local-field equations. Since Parker's calculation seems more reliable, the values α_T=2.20 Å³ and α₀=0.86 Å³ are used in the discussion from here on.

On the basis of the analysis in Sec. II, the isotropic solution is in fact the correct one, in spite of the fact that this value of α_T is an order of magnitude greater than the usually quoted free-ion values. As was pointed out previously,⁹ the crystalline symmetry of rutile is such that when the electric field is applied in the direction of the *c* axis, the polarizations of the titanium ions equal each other as do those of all the oxygen ions. When the field is applied perpendicular to the *c* axis, the polarizations of the titanium ions as well as those of the oxygen ions are again equal in the direction of the field, while the cross polarizations cancel. In the special case when the field is applied in the [110] or [110] directions, the cross polarizations vanish. Consequently, one may conclude from this that any localized electric dipole contributions to the total polarization cancel in rutile, and, therefore, the macroscopic electronic polarization of rutile is uniquely determined by the directionally independent contributions to the polarizabilities of the ions.

While the electric dipole moments of the oxygen ions in the absence of an external field cannot be determined from the macroscopic properties of the rutile crystal, the isotropic solution of the local-field equations gives the magnitude of the oxygen polarization induced by the applied field, which is also independent of direction. It is evident that this conclusion is in strong disagreement with the usual view that the polarization in oxide ma-

¹¹ It is important to note that three of the four equations (12) of Ref. 9 concerning the local fields when the applied field is in the *x* direction contain misprints. In particular, the first equation should contain as a contribution $P_{3z}2(f_{13zx} + f_{23zx})$ rather than $P_{3z}2(f_{13zx} + f_{14zx})$; the third equation should contain $P_{3z}(f_{11xz} + f_{34xz} + f_{35xz} + f_{35yz})$ rather than $P_{3z}(f_{11xz} + f_{34xz} + f_{35xz} + f_{35yz})$; and the fourth equation should contain $P_{3z}(f_{11xz} + f_{34xz} - f_{35yz} - f_{35xz})$ rather than $P_{3z}(f_{11xz} + f_{34xz} - f_{35xz} - f_{35yz})$.

⁸ *International Tables for X-ray Crystallography* (Kynoch Press, Birmingham, England, 1952), Vol. I, p. 236.

⁹ R. A. Parker, *Phys. Rev.* **124**, 1713 (1961).

¹⁰ H. C. Bolton, W. Fawcett, and I. D. C. Gurney, *Proc. Phys. Soc. (London)* **80**, 199 (1962).

terials such as rutile is due mostly to the contribution of the oxygen ions, while the cations are assigned their nominal free-ion polarizabilities, which are usually comparatively small in magnitude. That the polarizability of the titanium ion in rutile is an order of magnitude larger than its free-ion value may seem to be a remarkable conclusion, but it is shown in the next two sections that this result is in agreement with the analysis and conclusions reached in I.

IV. CORRELATION OF THE IONIC SIZES AND POLARIZABILITIES

By application of the Thomas-Kuhn sum rule, it was demonstrated in I that a simple approximate relationship exists between the quantity

$$R^2 = \sum_{\gamma'} |\langle \gamma | X + Y + Z | \gamma' \rangle|^2$$

for an ion, where X , Y , and Z are the sum of its electronic x , y , and z coordinates, and its electronic polarizability α . In particular, the relationship between the polarizabilities of two different ions, α_1 and α_2 , and the quantities R_1 and R_2 is given by

$$\alpha_1/\alpha_2 \approx R_1^4 n_2 / R_2^4 n_1, \quad (12)$$

where n_1 and n_2 are the number of electrons in these two different ions. If an ion has no electric dipole moment, i.e., if

$$\langle \gamma | X | \gamma \rangle = \langle \gamma | Y | \gamma \rangle = \langle \gamma | Z | \gamma \rangle = 0,$$

then

$$R^2 = \langle \gamma | X^2 | \gamma \rangle + \langle \gamma | Y^2 | \gamma \rangle + \langle \gamma | Z^2 | \gamma \rangle,$$

so that the quantity R may be used as a convenient measure of the extension of the ion.

As discussed previously, the titanium ion occupies a position possessing inversion symmetry in rutile, while the oxygen ion does not. Equation (12) may still be applied to a discussion of these two ions, however, if the induced polarization in the oxygen ion resulting from its lattice environment is not excessively large, and its contribution to the extension of the ion can be estimated.

Some information regarding the relative extensions of ions in a crystal may be obtained from a Fourier projection of its electron density determined for x-ray analysis. Determination of the shapes and, to a lesser extent, the sizes of ions lie near or possibly beyond the limit of accuracy of x-ray techniques at the present time. In particular, the truncation effect, caused by the fact that only a limited number of reflections are observable, limits the number of terms which can be determined in a Fourier expansion of the electron density.¹² This can result in pronounced distortions in the calculated electron density. Moreover, it is apparent that Eq. (12) gives the ratio of the ionic radii as a very

slowly varying function of the ratio of the polarizabilities, so that the radii are insensitive to large variations in the estimates of these quantities. In spite of these difficulties, it is believed that analysis of an electron density map for rutile can distinguish between two estimates for the polarizability of the titanium ion which differ by an order of magnitude. In particular, if one estimates that $\alpha_T = 0.20 \text{ \AA}^3$, then both the equations of Parker and BFG yield a value for α_0 in the c direction of approximately 2.4 \AA^3 . Noting that $n_T = 18$ and $n_0 = 10$, one finds that this estimate yields an R_0 almost twice as great as R_T . On the other hand, the correctness of the estimate $\alpha_T = 2.2 \text{ \AA}^3$ and $\alpha_0 = 0.86 \text{ \AA}^3$ results in an R_T which is actually larger than R_0 by some 45%—a result quite contrary to the usually accepted picture.

A Fourier projection of the electron density of rutile on the (001) plane has recently been published by Baur.¹³ While it is difficult to estimate the accuracy of such a map, it is of interest to examine its main features in an attempt to obtain the type of information discussed above. First, it is evident that the electron density of the oxygen ion is more extended toward the titanium ion than at right angles to this direction. This is entirely plausible in view of the anisotropic distorting influence which the lattice environment has on the oxygen ion. More important, however, is the fact that the extension of the titanium ion on this map is equal to or somewhat greater than that of the oxygen ion.

With specific reference to the two estimates of the polarizability discussed earlier, the titanium-oxygen separation of 1.96 \AA means that if the estimate $\alpha_T = 0.20 \text{ \AA}^3$ is correct, then according to (12) the extension of the titanium ion is only 0.75 \AA , a value slightly greater than the Pauling ionic radius. If the value $\alpha_T = 2.2 \text{ \AA}^3$ is correct, however, the extension is instead about 1.15 \AA . Figure 1 shows a reproduction of Baur's Fourier projection with the relevant titanium radii marked off on it. The 0.75-\AA radius lies wholly beneath the solid $2.0 e\text{\AA}^{-2}$ contour on the map. It is evident that this radius is well within the region in which the titanium ion is well defined. On the other hand, the dotted arc of 1.15-\AA radius traverses a region of minimum electron density and consequently seems to be more representative of the extension of the titanium ion. The only exception to this is in the small region along the line joining the titanium and oxygen nuclei in which the oxygen electron density is appreciable. As concluded previously, this is a result of the induced electric dipole moment in the oxygen ion resulting from its anisotropic lattice environment. Since the quantity R can be used as a measure of the extensions of the ions only if the effect of any such dipole moment is discounted, it is evident that this rise in the oxygen electron density does not in itself place any doubt on the value of 1.15 \AA for the extension of the titanium ion.

One may conclude then that, within the limitations

¹² See, for example, H. Lipson and W. Cochran, *The Determination of Crystal Structures* (G. Bell and Sons Ltd., London, 1955) for a detailed discussion of the inaccuracies involved.

¹³ W. H. Baur, *Acta Cryst.* **9**, 515 (1956).

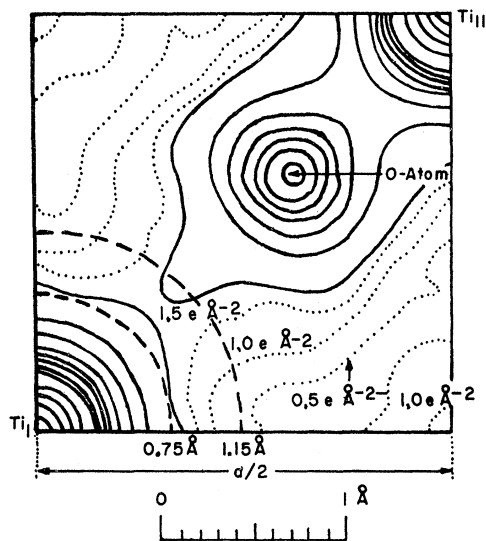


FIG. 1. Fourier projection of the electron density of rutile on the (001) plane (after W. H. Baur¹²). The dotted arc of radius 0.75 Å would be the radius for the Ti⁴⁺ ion if its polarizability were 0.2 Å³. It may be seen that the circular arc of 1.15-Å radius corresponding to a polarizability of 2.2 Å³ is much more representative of the extension of the titanium ion.

of the accuracy of electron-density determinations mentioned above, the analysis of the electron-density map of rutile strongly confirms the conclusion reached in the study of the local-field equations, namely, that the titanium ion does have a very large polarizability of 2.2 Å³ in the rutile crystal.

V. ORIGIN OF THE LARGE TITANIUM ION POLARIZABILITY

The conclusion that the polarizability of the titanium ion is an order of magnitude greater than the free-ion value is in qualitative agreement with the conclusion of I, namely, that the effect of the Madelung potential can greatly increase the polarizability of a cation in a crystal. This is demonstrated by the theoretical relationship derived in I between the free-cation polarizability α_f^+ and its value in the crystal α_c^+

$$\alpha_f^+/\alpha_c^+ = (\bar{E}_f^+ - eV_M)^2 / (\bar{E}_f^+)^2, \quad (13)$$

which gave favorable agreement with empirically determined cation polarizabilities in the alkali halides. Here V_M is the Madelung potential at the cation site and \bar{E}_f^+ is the mean excitation energy of the first kind for the free ion defined in I and given by the relation

$$(\bar{E}_f^+)^2 = e^2 h^2 n / 4\pi^2 m \alpha_f^+, \quad (14)$$

where n is the number of electrons in the ion. It is apparent that, according to (13), the cation polarizability can be profoundly influenced by a large Madelung potential.

At this point, it is of interest to apply Eq. (13) to a quantitative estimate of the effect upon the titanium

polarizability of the Madelung potential in rutile. The Madelung energy of rutile was calculated by means of the Ewald procedure by Bollnow,¹⁴ who expressed the result as a sum of six parameters associated with the six different lattice sites in the unit cell. Each of these parameters is in turn a sum of two infinite summations. The Madelung energy as well as the electrostatic potentials at the cation and anion sites are proportional to linear combinations of these six parameters. Unfortunately, Bollnow in giving the result for the Madelung energy listed the values of only two of these six parameters. Because of this, the infinite summations for the other four parameters had to be reevaluated.¹⁵

The magnitude of the Madelung potentials at the cation and anion sites in rutile were found to be greatly different. This difference may be summarized in the following way. The molar Madelung energy of a crystal is given by

$$U_M = \frac{1}{2} \sum_{i,j}^M e_i e_j / r_{ij} = \beta^2 e^2 N A_{\delta_0} / \delta_0, \quad (15)$$

where e_i and e_j are the net charges of the i th and j th ions, r_{ij} is their separation, β is the least common factor in the valences of the ions, A_{δ_0} is the Madelung constant associated with a characteristic equilibrium separation δ_0 , and N is Avogadro's number. The left side of Eq. (15) may be rewritten

$$\frac{1}{2} \sum_{i,j}^M e_i e_j / r_{ij} = \frac{1}{2} \sum_i^M e_j \sum_i^M e_i / r_{ij} = \frac{1}{2} \sum_j^M e_j V_j, \quad (16)$$

where V_j is the Madelung potential at the j th lattice site. For rutile, this expression becomes

$$\begin{aligned} \frac{1}{2} \sum_j^M e_j V_j &= \frac{N}{2} (e_{\text{Ti}} V_{\text{Ti}} + 2e_{\text{O}} V_{\text{O}}) = \frac{Ne}{2} (4V_{\text{Ti}} - 4V_{\text{O}}) \\ &= Ne\beta^2 \frac{(V_{\text{Ti}} - V_{\text{O}})}{2}, \end{aligned} \quad (17)$$

where V_{Ti} and V_{O} are the Madelung potentials at titanium and oxygen ion sites, respectively. Comparison of the right-hand sides of (15) and (17) indicates that the mean Madelung potential at a lattice site in rutile is given by

$$\frac{1}{2} (V_{\text{Ti}} - V_{\text{O}}) = V_{\text{av}} = eA_{\delta_0} / \delta_0. \quad (18)$$

The nearest-neighbor distance in rutile is 1.96 Å, while the corresponding Madelung constant is 4.816. Therefore, the quantity eV_{av} is equal to 35.4 eV. It was found that $V_{\text{Ti}} = 1.264 V_{\text{av}}$ while $V_{\text{O}} = -0.736 V_{\text{av}}$. Conse-

¹⁴ O. F. Bollnow, Z. Physik 33, 741 (1925).

¹⁵ The following misprints were found in the equations for these sums printed on p. 750 of Bollnow's paper. The sum D_2 should contain $G(\delta R_a)$ rather than $G(\delta R_c)$; the sum E_2 should contain $G(\delta R_a)$ rather than $G(\delta R_c)$; and the sum F_1 should contain the factor $\cos 2\pi\gamma(l_1 - l_2)$ rather than $\cos 2\pi(l_1 - l_2)$.

quently, the value of eV_{T_1} is 44.8 eV while that of eV_0 is -26.1 eV.

Since the magnitude of the Madelung potential in rutile is much greater at a cation site than at an anion site, its effect upon the cation polarizability is quite pronounced. The value of the free-cation polarizability α_f^+ necessary to produce the value of 2.2 \AA^3 in the crystal is, according to (13), equal to 0.32 \AA^3 when V_M is 44.8 eV. This is somewhat larger than the values usually given for the Ti^{4+} ion which approximately range between 0.2 and 0.3 \AA^3 . However, the agreement is good enough to indicate that the analysis of I, which is based on a purely ionic model, is quantitatively consistent with the result obtained from the analysis of the local-field equations, particularly in view of the simplifying approximations used in arriving at the theoretical relationship (13).

VI. CONCLUSIONS

The theoretical analysis developed in I for the study of ionic crystals coupled with a detailed study of the crystal symmetry of rutile has led to the conclusion that the isotropic solution of the local-field equations for rutile is the correct solution. This conclusion is supported experimentally by the isotropic nature of the magnetic susceptibility of rutile. The isotropic solution gives a value for the titanium ion polarizability an order of magnitude larger than the free-ion values usually assigned to this ion in crystals. This result is supported by a correlation of the ionic sizes as obtained from an electron density map with their polarizabilities in a manner described in I. Moreover, this result is in reasonably good quantitative agreement with a theoretical prediction of the effect of the crystalline interaction on the cation polarizability discussed in I.

This study gives a specific example of a situation which, as was inferred in I, can result in a cation polarizability becoming many times its free-ion value in a crystal. It is believed that studies of other materials can give similarly startling examples of the invalidity of the additivity rule for electronic polarizabilities of ions in crystals. Moreover, it is also apparent that the additivity rule for ionic sizes is also invalid, although not in such an obvious manner. In general, the ionic size is a slowly varying function of the magnitude of the crystalline potential, although in this case the size of the titanium ion is more than 50% greater than the usually accepted Pauling radius. Moreover, the oxygen ion, because of its relative instability, is highly susceptible to the magnitude of the distorting influence acting upon it, and is obviously a poor choice for a standard upon which to base the radii of ions according to the additivity rule.

These conclusions are, of course, greatly different from the usually held concepts regarding ions in crystals. It is hoped that this work will be of value in lending further understanding to the nature of ionic properties in crystals.

APPENDIX A. RELATIONSHIP BETWEEN $\langle \gamma | \mathbf{L}^2 | \gamma \rangle$ AND THE $\langle \gamma | \mathbf{L}_i^2 | \gamma \rangle$ FOR IONIC CRYSTALS HAVING INVERSION SYMMETRY

It is convenient in this discussion to proceed as in I and consider an orthogonalized basis set of ionic wave functions. This is because of the fact that the demonstration for a set of overlapping natural ionic wave functions, though similar to that for an orthogonalized set, is considerably more involved because of the much greater number of integrals which must be considered.

As was discussed in I, the one- and two-particle density matrices for a system described by a generalized antisymmetric product of orthogonalized ionic wave functions are given by

$$\gamma(\mathbf{x}_1' | \mathbf{x}_1) = \sum_{i=1}^M \gamma_i^{(n_i)}(\mathbf{x}_1' | \mathbf{x}_1), \quad (A1)$$

$$\begin{aligned} \Gamma(\mathbf{x}_1' \mathbf{x}_2' | \mathbf{x}_1 \mathbf{x}_2) &= \sum_{i=1}^M \Gamma_i^{(n_i)}(\mathbf{x}_1' \mathbf{x}_2' | \mathbf{x}_1 \mathbf{x}_2) \\ &+ \sum'_{i,j=1}^M \gamma_i^{(n_i)}(\mathbf{x}_1' | \mathbf{x}_1) \gamma_j^{(n_j)}(\mathbf{x}_2' | \mathbf{x}_2) \\ &- \sum'_{i,j=1}^M \gamma_i^{(n_i)}(\mathbf{x}_1' | \mathbf{x}_2) \gamma_j^{(n_j)}(\mathbf{x}_2' | \mathbf{x}_1). \end{aligned} \quad (A2)$$

The expectation value of \mathbf{L}_x^2 is given by

$$\langle \gamma | \mathbf{L}_x^2 | \gamma \rangle = \sum_{i=1}^N \langle \gamma | L_{x_i^2} | \gamma \rangle + \sum'_{i,j=1}^N \langle \gamma | L_{x_i} L_{x_j} | \gamma \rangle, \quad (A3)$$

which, making use of (A1) and (A2), may be written

$$\begin{aligned} \langle \gamma | \mathbf{L}_x^2 | \gamma \rangle &= \sum_{i=1}^M \int L_{x_1^2} \gamma_i^{(n_i)}(\mathbf{x}_1' | \mathbf{x}_1) d\mathbf{x}_1 \\ &+ \sum_{i=1}^M \int L_{x_1} L_{x_2} \Gamma_i^{(n_i)}(\mathbf{x}_1' \mathbf{x}_2' | \mathbf{x}_1 \mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \\ &+ \sum'_{i,j=1}^M \int L_{x_1} L_{x_2} \gamma_i^{(n_i)}(\mathbf{x}_1' | \mathbf{x}_1) \gamma_j^{(n_j)}(\mathbf{x}_2' | \mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \\ &- \sum'_{i,j=1}^M \int L_{x_1} L_{x_2} \gamma_i^{(n_i)}(\mathbf{x}_1' | \mathbf{x}_2) \gamma_j^{(n_j)}(\mathbf{x}_2' | \mathbf{x}_1) d\mathbf{x}_1 d\mathbf{x}_2. \end{aligned} \quad (A4)$$

The first two terms of (A4) comprise $\sum_{i=1}^M \langle \gamma | \mathbf{L}_{i_x^2} | \gamma \rangle$. The third term is a double sum of terms of the form

$$\int L_{x_1} \gamma_i^{(n_i)}(\mathbf{x}_1' | \mathbf{x}_1) d\mathbf{x}_1 \int L_{x_2} \gamma_j^{(n_j)}(\mathbf{x}_2' | \mathbf{x}_2) d\mathbf{x}_2,$$

which is a product of the net orbital moments of the i th and j th ionic constituents. By the argument of footnote 3, the probability amplitudes of all the ionic constituents are nondegenerate, so that their orbital moments vanish. Consequently, the third term vanishes. The final

term involves a sum of integral products of the type

$$\int L_{x_1} S_{ij}(\mathbf{x}_1) d\mathbf{x}_1 \int L_{x_2} S_{ij}(\mathbf{x}_2) d\mathbf{x}_2,$$

where $S_{ij}(\mathbf{x}_1)$ is an overlap integral for the ionic wave functions ψ_i and ψ_j in which the integration is over all electronic coordinates except the only common one, \mathbf{x}_1 . If one notes that $L_{x_1} = -i\hbar[x_1(\partial/\partial y_1) - y_1(\partial/\partial x_1)]$, then it is evident that the integrals $\int x_1(\partial/\partial y_1) S_{ij}(\mathbf{x}_1) d\mathbf{x}_1$ and $\int y_1(\partial/\partial x_1) S_{ij}(\mathbf{x}_1) d\mathbf{x}_1$ vanish because of the inversion symmetry of the system, since for every contribution to the integrals at the points $+x_1$ and $+y_1$, there is a contribution of equal magnitude to a similar integral at $-x_1$ and $-y_1$. As a result, the final term also vanishes.

When one carries through this argument for the y and z components also, one concludes that

$$\langle \gamma | \mathbf{L}^2 | \gamma \rangle = \sum_{i=1}^M \langle \gamma | \mathbf{L}_i^2 | \gamma \rangle$$

for an ionic crystalline system having inversion symmetry, which is the desired result.

APPENDIX B. THE DIRECTIONAL INDEPENDENCE OF THE ELECTRONIC SUSCEPTIBILITIES OF IONIC CRYSTALS

According to the previous discussion, the directional independence of the electronic susceptibilities rests upon the directional independence of infinite sums of the form

$$\sum_{\gamma' \neq \gamma} \langle \gamma | A_q | \gamma' \rangle^2$$

and

$$\sum_{\gamma' \neq \gamma} |\langle \gamma | A_q | \gamma' \rangle|^2 / E_{\gamma' \gamma},$$

where A_q is the operator associated with the susceptibility in question and q pertains to its directional component. It is demonstrated below that the directional independence of both of these sums is assured by the directional independence of a sum of the type

$$\sum_{\gamma' \neq \gamma} \langle \gamma | A_q | \gamma' \rangle \langle \gamma' | F_q | \gamma \rangle.$$

In addition, the validity of the assumptions necessary to prove that this sum is independent of direction is discussed.

The relationship between two directional components of an operator \mathbf{A} is given by the unitary transformation

$$A_{q'} = \mathbf{U}^{-1} A_q \mathbf{U}, \quad (\text{B1})$$

where $\mathbf{U}^{-1} = \mathbf{U}^\dagger$ is a unitary operator. The proof of the directional independence of the sum

$$\sum_{\gamma' \neq \gamma} \langle \gamma | A_q | \gamma' \rangle \langle \gamma' | F_q | \gamma \rangle$$

is based upon the assumption that the excited states of

the system may be placed into groups such that the matrix formulation of any transformation of the type (B1), namely,

$$\langle nm | A_{q'} | n'm' \rangle = \sum_{m'', m'''} \langle nm | \mathbf{U} | nm'' \rangle \langle nm'' | A_q | n'm''' \rangle \times \langle n'm''' | \mathbf{U} | n'm' \rangle \quad (\text{B2})$$

is valid. Here m is the index of a particular state in the group of states labeled by the index n . The validity of this assumption is discussed further on.

The proof of the directional independence of the sum in question is identical to that discussed in Ref. 2 for the special case in which $F_q = A_q$. In particular, since

$$\begin{aligned} & \sum_{m, m'} \langle nm | A_{q'} | n'm' \rangle \langle n'm' | F_{q'} | nm \rangle \\ &= \sum_{m, m', m'', m''', m^{iv}, m^v} \langle nm | \mathbf{U} | nm'' \rangle \langle nm'' | A_q | n'm''' \rangle \\ & \quad \times \langle n'm''' | \mathbf{U} | n'm' \rangle \times \langle n'm' | \mathbf{U} | n'm^v \rangle \\ & \quad \times \langle n'm^v | F_q | nm^{iv} \rangle \times \langle nm^{iv} | \mathbf{U} | nm \rangle, \quad (\text{B3}) \end{aligned}$$

and applying the properties of the unitary matrices

$$\sum_m \langle nm | \mathbf{U} | nm'' \rangle \langle nm^{iv} | \mathbf{U} | nm \rangle = \delta(m'', m^{iv}), \quad (\text{B4})$$

$$\sum_{m'} \langle n'm' | \mathbf{U} | n'm^v \rangle \langle n'm''' | \mathbf{U} | n'm' \rangle = \delta(m^v, m'''), \quad (\text{B5})$$

we then find that

$$\begin{aligned} & \sum_{m, m'} \langle nm | A_{q'} | n'm' \rangle \langle n'm' | F_{q'} | nm \rangle \\ &= \sum_{m'', m'''} \langle nm'' | A_q | n'm''' \rangle \langle n'm''' | F_q | nm'' \rangle. \quad (\text{B6}) \end{aligned}$$

Summing both sides of (B6) over all $n' \neq n$, we conclude that

$$\begin{aligned} & \sum_{\gamma' \neq \gamma} \langle \gamma | A_{q'} | \gamma' \rangle \langle \gamma' | F_{q'} | \gamma \rangle \\ &= \sum_{\gamma' \neq \gamma} \langle \gamma | A_q | \gamma' \rangle \langle \gamma' | F_q | \gamma \rangle. \quad (\text{B7}) \end{aligned}$$

The ground state has been excluded from the sum since, in the case of the ionic crystals, it is nondegenerate and the unitary transformation matrix reduces to a trivial phase factor. The exclusion is therefore necessitated by the fact that the ground-state matrix elements will not be the same in general.

For the special case $F_q = A_q$, the validity of the above proof assures the directional independence of the sum

$$\sum_{\gamma' \neq \gamma} |\langle \gamma | A_q | \gamma' \rangle|^2.$$

However, it is evident that the sum

$$\sum_{\gamma' \neq \gamma} |\langle \gamma | A_q | \gamma' \rangle|^2 / E_{\gamma' \gamma}$$

needs further consideration since, for example, if it is

rewritten as

$$(1/\bar{E}) \sum_{\gamma' \neq \gamma} |\langle \gamma | A_q | \gamma' \rangle|^2,$$

the quantity $(1/\bar{E})$ may be dependent upon the direction.

It is easily demonstrated, given (B7), that the directional independence of the sum

$$\sum_{\gamma' \neq \gamma} \langle \gamma | A_q | \gamma' \rangle^2 / E_{\gamma' \gamma}$$

is assured by the existence of an operator F_q having the property

$$A_q | \gamma \rangle = (\mathbf{H} F_q - F_q \mathbf{H}) | \gamma \rangle, \quad (\text{B8})$$

where \mathbf{H} is the Hamiltonian of the system not under the influence of an external field. It follows from (B8) that

$$\langle \gamma' | A_q | \gamma \rangle = E_{\gamma' \gamma} \langle \gamma' | F_q | \gamma \rangle. \quad (\text{B9})$$

Consequently,

$$\sum_{\gamma' = \gamma} |\langle \gamma | A_q | \gamma' \rangle|^2 / E_{\gamma' \gamma} = \sum_{\gamma' \neq \gamma} \langle \gamma | A_q | \gamma' \rangle \langle \gamma' | F_q | \gamma \rangle, \quad (\text{B10})$$

so that the directional independence of the left-hand side of (B10) is assured.

The existence of F_q is demonstrated by noting that $\langle \gamma' | \gamma'' \rangle = \delta(\gamma', \gamma'')$ and rewriting the sums in the following manner:

$$\begin{aligned} \sum_{\gamma'} \frac{\langle \gamma | A_q | \gamma' \rangle \langle \gamma' | A_q | \gamma \rangle}{E_{\gamma' \gamma} - E_\gamma} \\ &= \sum_{\gamma'} \langle \gamma | A_q | \gamma' \rangle \langle \gamma' | F_q | \gamma \rangle \\ &= \sum_{\gamma'} \langle \gamma | A_q | \gamma' \rangle \langle \gamma' | \left\{ +a_0 | \gamma \rangle + \sum_{\gamma''} \frac{\langle \gamma | A_q | \gamma' \rangle}{E_{\gamma'' \gamma} - E_\gamma} | \gamma'' \rangle \right\} \\ &= - \sum_{\gamma'} \langle \gamma | A_q | \gamma' \rangle \langle \gamma' | \gamma^{(1)} \rangle, \end{aligned}$$

where a_0 is an arbitrary constant and $|\gamma^{(1)}\rangle$ is just the expression for the first-order wave function obtained from perturbation theory. It is evident that $F_q | \gamma \rangle = -|\gamma^{(1)}\rangle$.¹⁶ Consequently, the existence of F_q is guaranteed by the validity of the expansion used for the susceptibility associated with A_q obtained from perturbation theory. It is evident that F_q may be written explicitly as

$$F_q = a_0 + (|\gamma\rangle)^{-1} \sum_{\gamma'} \frac{\langle \gamma | A_q | \gamma' \rangle}{E_{\gamma' \gamma} - E_\gamma} | \gamma' \rangle. \quad (\text{B11})$$

¹⁶ This discussion parallels that of A. Dalgarno in *Quantum Theory*, edited by D. R. Bates (Academic Press Inc., New York, 1961), Vol. I. Dalgarno exhibits F_q as the solution of a differential equation which is used to evaluate the energy to various orders according to perturbation theory.

There now remains the task of analyzing the conditions under which the assumption embodied in (B2) is valid. The matrix element of the transformed operator $\langle nm | \mathbf{U}^{-1} A_q \mathbf{U} | n' m' \rangle$ may be rewritten $\langle \mathbf{U} n m | A_q | \mathbf{U} n' m' \rangle$ so that, in the evaluation of the matrix element, the transformation of the operator is equivalent to the use of a different linear combination of wave functions assigned to the group of excited states under consideration. It is apparent that the set of wave functions assigned to each group of states must be complete enough so that it is always possible to find a linear combination of the set which will correspond to the transformation desired.

An example of such a situation occurs when the system has spherical symmetry, in which case the excited states transform according to the irreducible representations of the full rotation group. In this case, the unitary transformation corresponds to taking a different linear combination of the l -fold degenerate wave functions associated with a given energy level. If the system has lower symmetry, such a grouping of wave functions allowing any possible unitary transformation may not be possible. However, if the Hamiltonian for the system can be written in the form

$$\mathbf{H} = \mathbf{H}_0 + \mathbf{H}', \quad (\text{B12})$$

where the eigenfunctions of \mathbf{H}_0 allow such a grouping and the effect of \mathbf{H}' on these states is small, then the eigenfunctions of \mathbf{H} also may be grouped in such a manner. In this case, the effect of \mathbf{H}' is to split the degeneracies and to specify the linear combination of functions to be assigned to each state. Neither of these processes destroys the possibility of performing any possible transformation of the type (B2).

In the crystalline solid, the zero-order excited-state wave functions may be constructed from atomic functions $\psi(\mathbf{r} - \mathbf{r}(n))$ localized about the lattice points in the form

$$\psi_{\mathbf{k}} = (1/N)^{1/2} \sum_n e^{i\mathbf{k} \cdot \mathbf{r}(n)} \psi(\mathbf{r} - \mathbf{r}(n)), \quad (\text{B13})$$

where $\psi_{\mathbf{k}}$ now has the translational symmetry of the lattice. The atomic functions, of course, may be grouped in the manner required by (B2) and are nonlocalized enough so that they will be subject to a periodic potential whose symmetry is determined by the crystal structure. Since, in general, the effect of the periodic potential is small enough so that it only determines which linear combinations of the atomic functions are consistent with the crystal symmetry and, in the one-electron approximation, broadens the associated levels into quasicontinuous bands, then a grouping of the states exists such that the transformation (B2) is always possible.